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Absorption spectra of cobalt-doped α-$ZnAl_2S_4$ spinel type single crystals

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The absorption properties of α-$ZnAl_2S_4$:Co spinel type crystals grown by chemical transport reactions method are investigated. The spectra are assigned to the electronic transitions of Co^{2+} ions located in tetrahedral sites. It is shown that the revealed three absorption spectral components are caused by the transitions from the ground state $^4A(^4F)$ to the excited $^4T_1(^4F)$, $^4T_1(^4P)$ and $^2A(^2G)$ states.

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1. Introduction

The wide bandgap ternary semiconducting compound $ZnAl_2S_4$, depending on the growth conditions, crystallizes into four different structures, including the cubic modification α-$ZnAl_2S_4$ that belongs to the normal spinel structure [1, 2]. For the first time optical properties of α-$ZnAl_2S_4$ crystals activated with a transition metal impurity (chromium) were studied in [3]. It was shown that Cr^{3+} ions, being located in the octahedral coordination of sulphur, exhibit a strong broad band emission in the near infrared spectral region (0.7-0.9 μm) at temperatures that exceed 500K [4]. Spectroscopic investigations of α-$ZnAl_2S_4$ doped with titanium were carried out in [5]. The obtained emission characteristics were assigned to the spectral bands arising from the ligand - Ti^{4+} charge transfer for octahedral sites of titanium.

In a number of oxide spinels the tetrahedral coordinated Co^{2+} ions are characterized by a strong luminescence in the visible and near infrared regions with very short lifetimes [6-8]. Optical properties of the tetrahedral Co^{2+} in the sulphur surrounding have been studied in [9, 10] and references therein, however, there are no papers on spectroscopic investigations of the cobalt doped sulphide spinels.

This paper investigates the absorption properties of Co^{2+} ions in α-$ZnAl_2S_4$:Co single crystals, yielding a determination of spectroscopic parameters of the activation impurity.

2. Experimental procedure

Bulk stoichiometric α-$ZnAl_2S_4$ crystals were grown by the chemical vapour transport method, using I_2 as a transport agent. The obtained samples, with an estimated Co-impurity concentration in the region of 0.1-0.3 at %, were optically homogeneous octahedrons with the dimensions of up to 10 mm^3 and (111) oriented mirror-like faces. In contrast to the undoped colourless α-$ZnAl_2S_4$ crystals, the Co-doped samples are orange coloured. The X-Ray analyses confirmed that all samples were crystallized into the normal spinel-type structure.

The optical absorption spectra for both undoped and Co-doped α-$ZnAl_2S_4$ were recorded at room temperature using a Perkin Elmer Lambda 900 spectrometer in the wavelength range of 300 – 2000 nm.

3. Results and discussion

The absorption spectra at room temperature of both undoped and Co-doped α-$ZnAl_2S_4$ are presented in Fig. 1. The short-wavelength edge at 0.35 μm (E_g(300 K) = 28230 cm^{-1}) for the undoped α-$ZnAl_2S_4$ sample corresponds to the intrinsic absorption (indirect band gap), being in a good agreement with the results obtained in [11]. The absorption spectrum of α-$ZnAl_2S_4$:Co crystals includes the impurity spectral bands located at about 1.6 μm ($E_{A1} \approx 6452$ cm^{-1}, quadruplet), 0.77 μm (E_{A2} =12985 cm^{-1}, triplet) and 0.48 μm (E_{A3} =20163 cm^{-1}, broad band). As to the absorption edge, for the doped samples it shifts by about 6452 cm^{-1} towards lower energies.

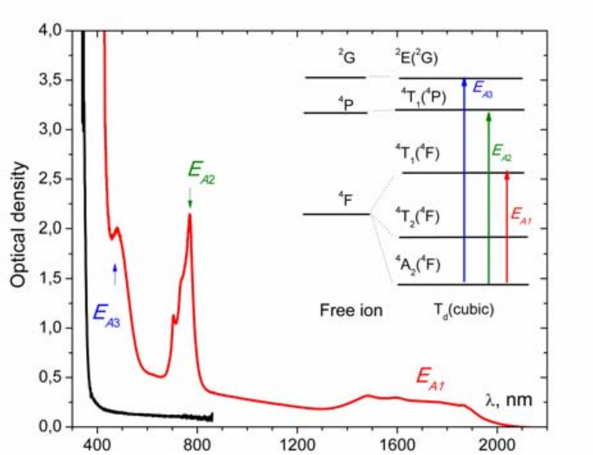

Fig. 1. Optical absorption spectra, energy level splitting and transitions for undoped and Co-doped α-$ZnAl_2S_4$ single crystals.

In fact, the observed impurity bands are quite similar to those reported for $MgAl_2S_4:Co^{2+}$ and $CaAl_2S_4:Co^{2+}$ [9], $MgAl_2O_4:Co^{2+}$ [12] and $ZnGa_2S_4:Co^{2+}$[10], where Co ions are in tetrahedral coordination.

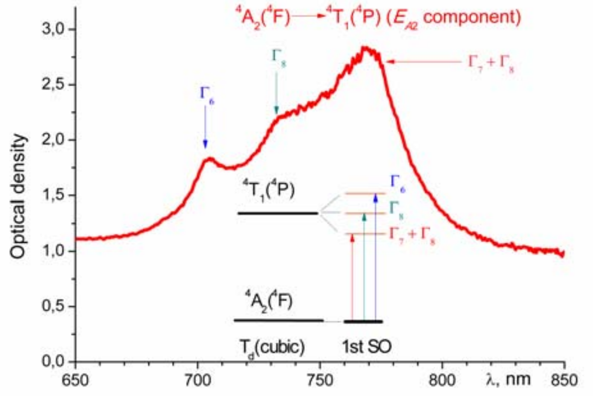

Fig. 2. The E_{A2} absorption component for Co-doped α-$ZnAl_2S_4$ single crystals and the transitions from the ground state $^4A_2(^4F)$ to the three sublevels of the excited one $^4T_1(^4P)$.

The E_{A2} absorption lines are ascribed to the spin and electric dipole allowed transitions $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$. Indeed, in $MgAl_2S_4:Co^{2+}$, $CaAl_2S_4:Co^{2+}$ [9] as well as in $ZnS:Co^{2+}$, where the impurity replaces only the tetrahedral coordinated Zn^{2+} ion [13], the similar absorption lines are located almost at the same energies Fig. 2. In conformity with the crystal field theory [14], the $^4T_1(^4P)$ state of the Co^{2+} ion sited in T_d symmetry splits into three sublevels Γ_6, Γ_8 and $\Gamma_7+\Gamma_8$ due to the first order of the spin – orbit coupling effects. Thus, the observed three peaks of the E_{A2} spectral component are assigned to the electron transitions from the ground state $^4A_2(^4F)$ to the three sublevels of the excited state $^4T_1(^4P)$. The energy of the spin-orbital coupling of the interaction between the total orbital angular momentum and the total spin momentum of the valence electrons, obeying the Russel – Saunders coupling scheme, is described by the relation:

$$W = \lambda(L,S)\frac{J(J+1) - L(L+1) - S(S+1)}{2} \tag{1}$$

where J, L, S are the quantum numbers and $\lambda(L,S)$ is the constant of the spin-orbit coupling. Thus, the energetical width of the multiplet $^4T_{1g}(^4P)$, i.e., the distance between $J=|L+S|$ and $J=|L-S|$, is:

$$\left.\begin{array}{ll} \Delta W = \lambda(L,S)\,S(2L+1) & if\;\; L \geq S \\ \Delta W = \lambda(L,S)\,L(2S+1) & if\;\; L \leq S \end{array}\right] \tag{2}$$

The energetical distance between the terms of the multiplet is ΔW = 1286 cm^{-1} (see Table 1), and knowing that the quantum numbers for the term $^4T_{1g}(^4P)$ term are $L=1$, $S=3/2$, it is possible to calculate the constant of the spin-orbit coupling:

$$\lambda(L,S) = \frac{\Delta W}{L(2S+1)} = \frac{1286\,(cm^{-1})}{4} \approx 321\,(cm^{-1}) \tag{3}$$

Table 1. Energies of the spectral components of the absorption spectra of Co^{2+} ions in α-$ZnAl_2S_4$ spinel and their assignments.

Absorption		
Energy, cm^{-1}		Assignment
		$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$
E_{A1}	5355	$^4A_2(^4F) \rightarrow \Gamma_6$
	5645	$^4A_2(^4F) \rightarrow \Gamma_8$
	6250	$^4A_2(^4F) \rightarrow \Gamma_7$
	6742	$^4A_2(^4F) \rightarrow \Gamma_8$
		$^4A_2(^4F) \rightarrow {}^4T_1(^4P)$
E_{A2}	12985	$^4A_2(^4F) \rightarrow \Gamma_7+\Gamma_8$
	13614	$^4A_2(^4F) \rightarrow \Gamma_8$
	14180	$^4A_2(^4F) \rightarrow \Gamma_6$
E_{A3}	20728	**$^4A_2(^4F) \rightarrow {}^2A_1(^2G)$**
E_{A4}	23212	**$^4A_2(^4F) \rightarrow {}^2T_2(^2G)$**

The E_{A1} IR component consists of at least four lines, Fig. 3, ascribed to the $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transition. By following the same procedure, as described for the previous case, we estimated the constant of the spin-orbit coupling for the exited level $^4T_1(^4F)$ to be:

$$\lambda(L,S) \approx 189\,cm^{-1} \tag{4}$$

Both results are in good agreement with those obtained in [9, 10, 13] and are the confirmation that the ions of Co^{2+} are in the tetrahedral sulphur surrounding.

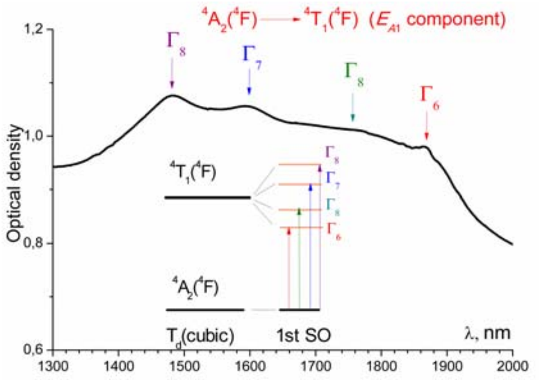

Fig. 3. The E_{A1} IR absorption component for Co-doped α-$ZnAl_2S_4$ single crystals and the transitions from the ground state $^4A_2(^4F)$ to the four sublevels of the excited one $^4T_1(^4F)$.

The quite intensive absorption within E_{A3} band is due to the fact that, in spite of the forbiddenness of the $^4A_2(^4F) \rightarrow {}^2A(^2G)$ transition, at the ligand field strength of Co^{2+} in T_d ($Dq \approx 400$ cm^{-1}) the $^4T_1(^4P)$ excited level is very close to the doublet states arising from the ^2G free-ion term and the spin orbit mixing of quartets and doublets, that relaxes the spin-forbidden transitions to these doublet states.

The long-wavelength shift of the absorption edge of the α-$ZnAl_2S_4$:Co crystals, with respect to the edge of the undoped samples, according to [10], could be attributed to an impurity energetic band that arises due to the formation of a solid solution between the dopant and the host lattice ($Zn_{(1-x)}Co_xGa_2S_4$). However, this is not our case, because in [10] the concentration of the dopant was quite large, up to 2% mol, i.e. about an order of magnitude higher than in our samples. Therefore, the observed "red shift" of the edge can be attributed to the long wavelength side of an intensive absorption broad band caused by the high energy optical transitions of the Co^{2+}-ions, perhaps $^4A_2(^4F) \rightarrow {}^2T_2(^2G)$.

4. Conclusions

Spinel-type single crystals of α-$ZnAl_2S_4$:Co^{2+} were grown by chemical transport reaction method. It is shown that the optical absorption spectral bands attributed to the Co^{2+} ions in the tetrahedral coordination of sulphur are similar to those of the cobalt doped oxide spinels host crystals, the former being shifted to the lower energies. The impurity absorption of α-$ZnAl_2S_4$:Co crystals caused by the $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ (E_{A2} component) and $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transitions (E_{A1} IR component) corresponds to the spectral region used in the fibre-optics communication systems, therefore this material could be of practical interest as a saturable absorber.

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References

[1] G. Steigmann, Acta Crystallographica **23**, 142 (1967).
[2] H. J. Berthold, K. Köhler, Zeitschrift für anorganische und allgemeine Chemie **475**, 45 (1981).
[3] T. Kai, M. Kaifuku, I. Aksenov, K. Sato, Japanese Journal of Applied Physics **34**, 3073 (1995).
[4] I. Broussell, E. Fortin, L. Kulyuk, S. Popov, A. Anedda, R. Corpino, Journal of Applied Physics **84**, 533 (1998).
[5] S. Anghel, G. Boulon, A. Brenier, E. Fortin, S. Klokishner, D. Koshchug, L. Kulyuk, K. Sushkevich, Journal of Physics: Condensed Matter **22**, 055903 (2010).
[6] J. F. Donegan, F. J. Bergin, G. F. Imbusch, J. P. Remeika, Journal of Luminescence **31-32**, 278 (1984).
[7] T. Abritta, F. H. Blak, Journal of Luminescence **48-49**, 558 (1991).
[8] K. Izumi, S. Miyazaki, S. Yoshida, T. Mizokawa, E. Hanamura, Physical Review B **76**, 075111 (2007).
[9] S. K. Oh, H. J. Song, W. T. Kim, H. G. Kim, C. I. Lee, T. Y. Park, M. S. Jin, C. S. Yoon, Journal of Physics and Chemistry of Solids **61**, 1243 (2000).
[10] H.-G. Kim, W.-T. Kim, Physical Review B **41**, 8541 (1990).
[11] O. V. Kulikova, N. A. Moldovyan, S. M. Popov, S. I. Radautsan, A. V. Siminel, Japanese Journal of Applied Physics Supplement **32-3**, 586 (1993).
[12] D. K. Sardar, J. B. Gruber, B. Zandi, M. Ferry, M. R. Kokta, Journal of Applied Physics **91**, 4846 (2002).
[13] H. A. Weakliem, The Journal of Chemical Physics **36**, 2117 (1962).
[14] S. Sugano, Y. Tanabe, H. Kamimura, Multiplets of Transition Metal Ions in Crystals. (Academic Press, New York, 1970).

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