

ments of emission spectra were carried out in 300 – 600 nm range under excitation in 225 nm wavelength. The PL thermal quenching in 345, 390 nm bands were measured in the heating and cooling modes at rate of $\beta = 1$ K/s in RT – 800 K temperature range.

It is shown that PL emission spectra have maximum at 350 nm band and PL intensity decreases with increasing temperature without changing the peak position, see Fig.1. It is demonstrated that PL spectra can be decomposed into three Gaussian components with $E_{\max} = 3.61, 3.28, 2.62$ eV and FWHM = 0.42, 0.70, 0.62 eV, respectively.

Semi-quantitative analysis of the experimental dependences of PL quenching was carried out within the Mott-Seitz formalism. It is shown that intensity decreasing in the investigated temperature range is characterized by two non-radiative relaxation channels with activation energies of $E_A = 0.27, 0.81$ and $0.22, 0.58$ eV in 345 and 390 nm bands, respectively. The possible mechanisms for observed quenching processes were discussed in frame of model representations of the oxygen-related complexes in different charged states.

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EFFECT OF IRON SUBSTITUTION BY COBALT ON THE CRYSTAL STRUCTURE AND PHASE TRANSITION OF $\text{Fe}_{7-y}\text{Co}_y\text{X}_8$ (X = S, Se) COMPOUNDS

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Iron sulfide Fe_7S_8 and iron selenide Fe_7Se_8 have NiAs-type layered superstructures with the ordering of vacancies in each second metallic layer. When the temperature increases, these compounds show first-order structural transitions from superstructures with ordered vacancies to the NiAs-type structure with vacancy disorder at the critical temperatures $T_t \approx 590$ K [1] and $T_t \approx 660$ K for Fe_7S_8 and Fe_7Se_8 , respectively. The present work is aimed to study the effect of the Co for Fe substitution on the crystal structure and phase transitions in $\text{Fe}_{7-y}\text{Co}_y\text{X}_8$ (X = S, Se) compounds.

The polycrystalline samples $\text{Fe}_{7-y}\text{Co}_y\text{X}_8$ with cobalt concentration ranging from $y = 0$ to $y = 7$ were synthesized by solid-state reactions in evacuated quartz ampoules. All substituted samples $\text{Fe}_{7-y}\text{Co}_y\text{X}_8$ were found to have a layered 3C-type superstructure of the NiAs-type. It was found that, the average interlayer distance characterized

by the c lattice parameter decreases significantly (about of 10 %) with increasing cobalt concentration, while the a lattice parameter remains nearly unchanged.

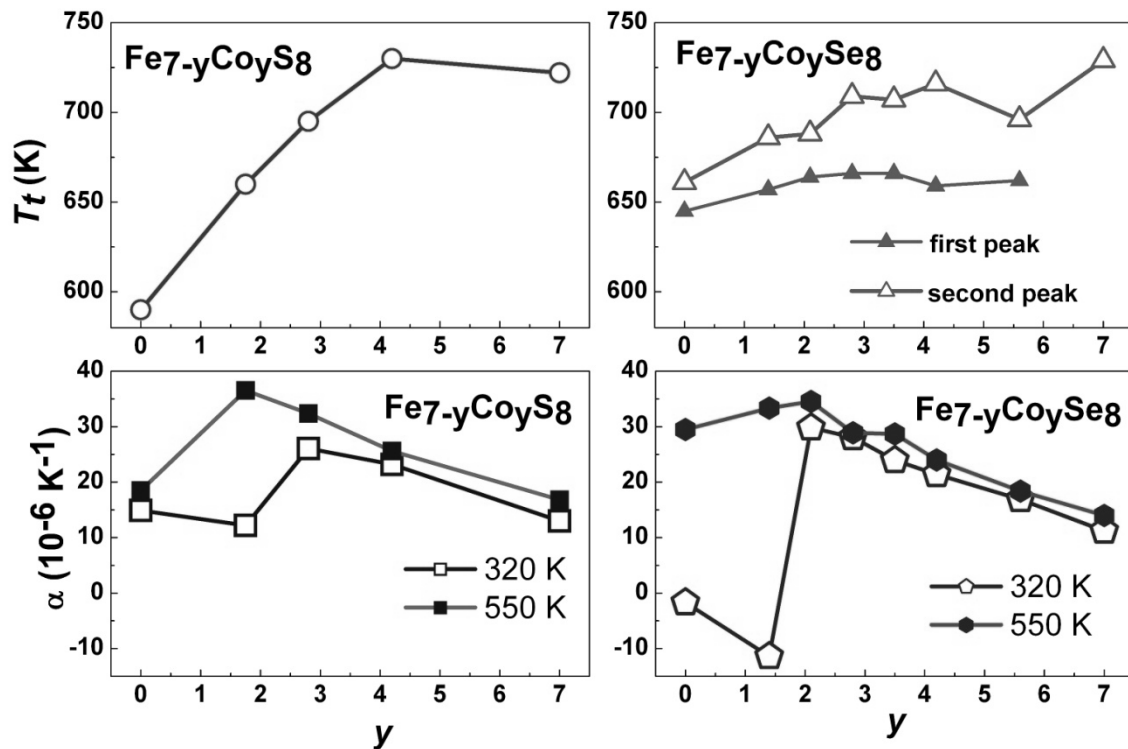


Fig. 1. The dependence of temperature of structural transition (T_t) and the coefficient of linear thermal expansion (α) on the cobalt concentration (y) in $\text{Fe}_{7-y}\text{Co}_y\text{S}_8$ and $\text{Fe}_{7-y}\text{Co}_y\text{Se}_8$ compounds

The structural transitions in the prepared samples were studied by measuring the temperature dependence of the coefficient α of the linear thermal expansion. It has been found that all samples exhibit structural transitions from superstructure with ordered vacancies to a 1C-type structure without ordering of vacancies. In the selenides $\text{Fe}_{7-y}\text{Co}_y\text{Se}_8$, this structure transition occurs in two steps (two neighbors peaks were observed in the $\alpha(T)$ curve); the first anomaly corresponds to the transition $3\text{C} \rightarrow 2\text{C}$ and the second anomaly is associated with the $2\text{C} \rightarrow 1\text{C}$ transition. The critical temperatures of structural transitions are found to increase with increasing cobalt concentration, as seen in figure 1. On the other hand, the value of coefficient of thermal expansion was found to decrease with the Co for Fe substitution, which can be explained by the increase of the binding energy and the stiffness of the lattice when the Co content increases. The reduced values of α observed at low Co concentrations ($y < 2$) are related to the influence of a long-range ferrimagnetic order in these compounds.

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