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Compressibility and electronic structure variation with pressure for $EuVO_4$: A combined experimental and computational study

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Europium orthovanadate, $EuVO_4$, crystallizes in the zircon-type structure (space group $I4_1/amd$, $Z = 4$) under ambient conditions and is known to transform to a scheelite-type structure at about 8 GPa. The equation of state of this compound has already been studied. However, the reported experimental and theoretical values of the bulk modulus exhibit a considerable scatter, for both, the zircon and schheelite-type polymorphs. As for the dependence of the electronic structure with pressure, such data have not been reported yet.

In the present study, structural, elastic and electronic properties of zircon-type and scheelite-type europium orthovanadate are investigated experimentally, by *in-situ* X-ray diffraction using synchrotron radiation, and theoretically within the framework of the density functional theory (DFT). The obtained results on bulk modulus show a perfect agreement of experiment with theory. Discrepancies between the present values and those earlier reported ones are attributed to differences in the details of the experimental procedure. The calculated band structure confirms that zircon-type europium orthovanadate is a direct-gap semiconductor, with a band-gap energy at zero pressure of 2.88 eV. The variation of electronic structure and of the bandgap with pressure is determined.

P-05

Energy transfer processes to Eu^{3+} ions in $K_5Li_2GdF_{10}$ doped with Eu^{3+}, Pr^{3+}, Tb^{3+} and Dy^{3+} upon VUV excitation

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The X-ray examination of small crystals of $K_5Li_2LnF_{10}$ *(*Ln = La−Gd*)* has proved that the materials crystallize in a form of single phase. It is orthorhombic (space group D_{2h}^{16}–*Pnma*), the unit-cell parameters are a = 20:775 Å; b = 7:882 Å; c = 6:963 Å; for Ln = La.

The crystal structure is built from layers perpendicular to the a axis, formed by LnF_8 dodecahedra and LiF_4 tetrahedra. Rare-earth ions and lithium ions occupy sites with C_S symmetry, whereas potassium and fluorine ions occupy sites with C_S and C_1 symmetry. The crystal structure is uncommon in that the LnF_8 polyhedra do not share fluorine ions and the nearest rare-earth ions are separated by more than 6.8 Å. Owing to these features, exchange interactions between rare-earth ions may be neglected and multipole interactions are expected to be strongly reduced. Such a conditions allows to analyze rather pure multipole interactions between ions. Pr^{3+}, Tb^{3+} and Dy^{3+} possesses metastable multiplets situated in the blue area of the spectrum that should transfer the energy to the low positioned Eu^{3+} $^5D_0$ one [1].

The Pr^{3+} ion can work as a sensitizer of Eu^{3+} luminescence from the $^5D_0$. It has been discovered that the Pr^{3+} ions to transfer an energy to the Eu^{3+} ions needs the presence of Gd^{3+} ions. In $K_5Li_2LaF_{10}$ system only a luminescence of Pr^{3+} was observed upon excitation of f-d bands of praseodymium [2]. It can suggest that excited the Pr^{3+} ions very efficiently transfer the energy to Gd^{3+} ions. Such an efficient energy transfer has been observed in other system YF_3:Pr^{3+}, Gd^{3+} [18]. At low temperature emission spectra (not shown here) the Pr^{3+} f–f emission upon UV–VUV excitation was observed. It suggests that energy transfer from d levels of Pr^{3+} to Gd^{3+} states is thermally dependent.

In the case of Dy^{3+} ions, no transfer upon excitation into f-d bands of Dy^{3+} was observed to Gd^{3+} or Eu^{3+} ions. Dysprosium is rather independent. As well as no transfer from Dy^{3+} to other ions was not observed, no efficient transfer to the $^4F_{9/2}$ multiplet of Dy^{3+} was observed.

The best results was found for Tb^{3+}+Eu^{3+} system. It occurs that upon excitation into f-d transitions bands of Tb^{3+} an efficient luminescence from Eu^{3+} can be observed in $K_5Li_2GdF_{10}$ an $K_5Li_2LaF_{10}$ matrixes. What is more upon excitation of Tb^{3+} ions below the d levels no efficient energy transfer from Tb to Eu was observed. Such an observation is validated with analysis of the decay curves of Tb^{3+} luminescence.

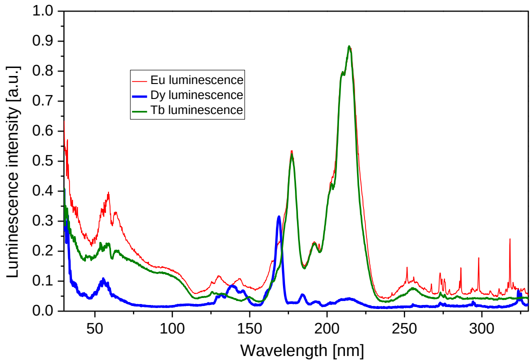

Figure 1.. Excitations spectra of luminescence recorded at Eu (red), Tb (blue), and Dy (blue) emission lines. The energy transfer from the Tb^{3+} ions to the Eu^{3+} one can be observed in the 150 – 275 nm region.

The $^5D_4$ multiplet lifetime of 10 at% terbium doped $K_5Li_2GdF_{10}$ is 7500 μs and is the same as in the Tb–Eu system.

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