

Optical spectra of solution of triflorides in melting fluorides lithium and sodium

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Abstract

In this article we show the optical spectra of Er(III) in LiF and NaF which were obtained in spectral analytical complex in the range of 6000-42000 cm⁻¹ (T = 1275-1325 K). It was found 11 f-f electronic transitions in LiF ⁴I_{15/2} → ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2}, ⁴F_{9/2}, ²H_{11/2}, ⁴F_{7/2}, ⁴F_{5/2}, ⁴F_{3/2}, ²H_{9/2}, ⁴G_{11/2}, ⁴G_{9/2}, but we are able to distinguish only 10. Both melting systems have 2 hypersensitive transitions ⁴I_{15/2} → ²H_{11/2} and ⁴I_{15/2} → ²G_{11/2}.

It was shown that the symmetry of groupings ErF₆³⁻ have influenced stronger on the intensity of f-f electronic transitions than the transfer of F- charge on Er(III). Taking into consideration (paying attention) to the isovalent isomorphism for the row of ions of rare earth elements in fluorides of alkali metals which were established (discovered) earlier by the Raman scattering and electronic spectroscopy methods. f-f Electronic transitions were assigned to the complex groupings ErF₆³⁻. The big influence of the 2d coordination sphere on the intensity of hypersensitive and non-hypersensitive transitions connected with the decrease of the symmetry of complex groupings ErF₆³⁻ in melting LiF in comparison with NaF. The main reason influenced on the intensities of f-f transition is the polarization from the cations of 2d coordination sphere on ErF₆³⁻. The very strong influence of 2d coordination sphere on intensities of electronic transitions of Er(III) was presented. This process is top in lithium melts where the effect of polarization of coordination sphere of Er(III) is the greatest.

References

- [1] Y.A. Barbanel. Coordination chemistry of f-elements in melts. *Moscow: Energoatomizdat*. **1985**. P.143. (russian)
- [2] A.A. Khokryakov, A.S. Payvin, S.I. Noritsyn. Spectral analytical complex for registration of electronic spectra of high-temperature melts and its borders of applicability. *Melts*. **2014**. Vol.1. P.62-70. (russian)
- [3] V.U. Shishkin, V.S. Mityaev. Refining of halogenides of alkali metals by the method of floating zone process. *Izvestiya of Academy of Science. USSR. Inorganic materials*. **1982**. No.11. P.1917-1918. (russian)
- [4] A.A. Khokryakov, A.O. Vershinin, A.S. Payvin, A.A. Lizin. Electronic spectra of Ce(III) and Pr(III) in melting fluorides of alkali metals. *Melts*. **2017**. Vol.3. P.226-235. (russian)
- [5] A.A. Khokryakov, A.O. Vershinin, A.S. Payvin, A.A. Lizin. Electronic spectra of Nd(III) in melting fluorides of alkali metals. *Melts*. **2015**. Vol.4. P.3-11. (russian)
- [6] W.T. Carnall, P.R. Fields, K. Rajnak. Spectral Intensities of the Trivalent Lanthanides and Aqua Ions I. Pr³⁺, Nd³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Tm³⁺. *J. Chem. Phys.* **1968**. Vol.49. No.10. P.4424-4442.
- [7] W.T. Carnall, G.L. Goodman, R. Rajnak, R.S. Rana. A Systematic analysis of the spectra of the lanthanides doped into single crystal LaF₃. *J. Chem. Phys.* **1989**. Vol.90. No.7. P.3443-3457.
- [8] V. Dracopoulos, B. Gilbert, G.N. Papatheodorou. Vibrational models and structure of lanthanide fluoride-potassium fluoride binary melts: LnF₃-KF (Ln = La, Ce, Nd, Sm, Dy, Yb). *J. Chem. Soc. Faraday Trans.* **1998**. Vol.94. P.2601-2604.
- [9] A.A. Khokryakov, A.O. Vershinin, A.S. Payvin, V.U. Shishkin. Electronic spectra of SmF₃ in melting fluorides of alkali metals. *Melts*. **2017**. Vol.2. P.175-182. (russian)
- [10] D.E. Henric, R.L. Fellows, G.R. Choppin. Hypersensitivity in the electronic transition of lanthanide and actinide complexes. *Coordination Chemistry Reviews*. **1976**. Vol.18. P.139-224.