Systematic crystal field studies of Mn^{4+}-doped perovskites

A.M. Srivastava[1], M.G. Brik[2]

[1] GE Global Research, Niskayuna, NY 12309, USA
[2] Institute of Physics, University of Tartu, Tartu 51014, Estonia

The deep red luminescence of the Mn^{4+} ($3d^3$ electron configuration; isoelectronic with the Cr^{3+} ion) ions finds commercial application in lighting and has the potential for use in numerous other applications, that is why the optical properties of these materials are the subject of thorough investigations.

Recently we have extensively studied the crystal field effects in various perovskite crystals doped with Mn^{4+} ions (1-3). Using the exchange charge model of crystal field, we could successfully calculate the splitting of the Mn^{4+} energy levels and assign all prominent features in the experimental emission and absorption spectra.

As an example of the performed analysis, we show in Fig. 1 the experimental absorption and emission spectra of $LaAlO_3$:Mn^{4+} together with the calculated Mn^{4+} energy levels (3). Good agreement between the calculated results and experimental spectra can be seen easily.
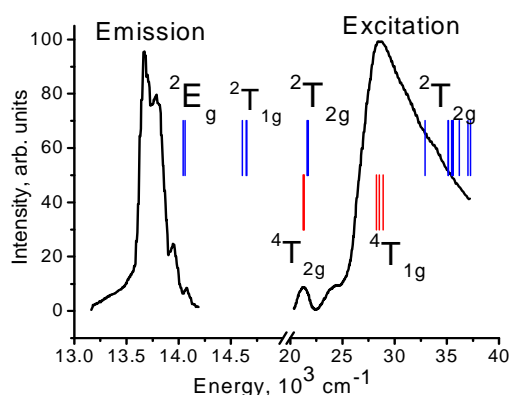

Fig. 1. Comparison of the experimental emission and excitation spectra (solid lines) with the calculated energy levels (vertical lines) of Mn^{4+} in $LaAlO_3$. See Ref. (3) for more details.

Special attention was paid to comparative cross-cutting studies of position of the emitting ^2E level of Mn^{4+} ions in different perovskites. According to the theory of Tanabe and Sugano, the peak emission wavelength of the spin-forbidden $^2E_g \rightarrow {}^4A_{2g}$ transition is singularly dependent on the covalence of the "Mn^{4+}-Ligand" bonding and is fairly independent of the strength of the crystalline field in a solid. This covalence of the metal-ligand bonding, which determines the energy of the Mn^{4+} $^2E_g \rightarrow {}^4A_{2g}$ emission transition, can be changed by changing the constitution (cations and anions) of the host lattice. To rationalize variation of energy of the $^2E_g \rightarrow {}^4A_{2g}$ emission, we introduced a non-dimensional parameter

$$\beta_1 = \sqrt{\left(\frac{B}{B_0}\right)^2 + \left(\frac{C}{C_0}\right)^2} , \qquad (1)$$

where the subscript "0" refers to the values of the Racah parameters for free ion (for Mn^{4+}, $B_0 = 1160$ cm^{-1} and $C_0 = 4303$ cm^{-1}), and B and C are the Racah parameters for Mn^{4+} ions in a given crystal.

Fig. 2 shows how the energy of the Mn^{4+} $^2E_g \rightarrow {}^4A_{2g}$

transition depends on the β_1 value for a number of the perovskites. As seen from Fig. 2, the peak emission energy of the $^2E_g \rightarrow {}^4A_{2g}$ transition in this group of perovskites is linearly related to β_1. This indicates that any description of the nephelauxetic effect for the Mn^{4+} containing hosts must consider both Racah parameters B and C and that the linking the ^2E_g state energy and the β_1 parameter allows for predicting the ^2E_g state position in various perovskites.
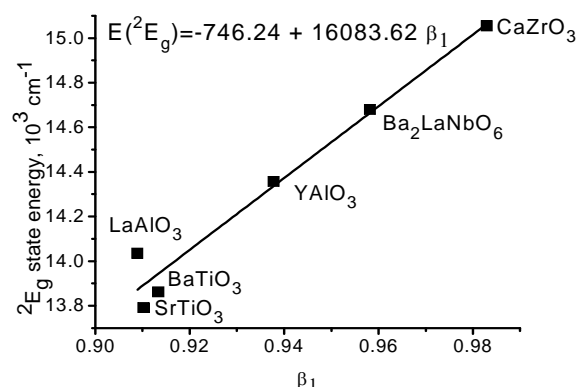

Fig. 2. The relation between the position of the Mn^{4+} ^2E_g level and β_1 (Eq. (1)). Equation of the linear fit is given in the graph.

We believe that the proposed relation between the energy of the Mn^{4+} $^2E_g \rightarrow {}^4A_{2g}$ transition and decreased (as a consequence of the nephelauxetic effect) Racah parameters B and C can help in prediction of the energy of the ^2E_g state and/or β_1 parameter in new hosts with tetravalent manganese ions. Further studies of the Mn^{4+}-doped materials are under way.

REFERENCES

1. A.M.Srivastava, M.G.Brik, *J. Lumin.* **132**, 579, (2012).
2. M.G.Brik, A.M.Srivastava, *J.Lumin.*, **133**, 69, (2013).
3. A.M.Srivastava, M.G.Brik, *Opt.Mater.* (2013, in press, http://dx.doi.org/10.1016/j.optmat.2013.03.021).