ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 3, pp. 527–532. © Pleiades Publishing, Ltd., 2015.
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Quantum-Chemical Prediction of the Luminescent Properties of $Eu_{0.33}Zr_2(PO_4)_3$

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Received October 2, 2014

Abstract—By an example of $Eu_{0.33}Zr_2(PO_4)_3$ phosphate, the possibility of predicting the luminescence in the framework of the time-dependent density functional theory (TD DFT) was demonstrated. The theoretical emission spectra of Eu^{3+} were computed on the basis of the cluster approach with the use of the sequential growth technique. The optimal cluster $[EuZr_2P_6O_{24}H_{18}]^{+11}$ and optimal basis set Eu[MWB52], Zr[MWB28], P[MWB10], O[6-31G(d,f)], H[6-31G] were determined. The deviation between the calculated and experimental wavelengths was less than 1%.

Keywords: time-dependent density functional theory (TD DFT), pseudopotentials, Nasicon, clusters, luminescence excitation spectrum, Eu^{3+} ion

DOI: 10.1134/S1070363215030020

The Eu^{3+} ion is known to be an active component of phosphorescent materials. In combination with other emitters it is widely used as a phosphor in, e.g., plasma displays, fluorescent lamps, and light-emitting diodes. Also, compounds based on Eu^{3+} find application as materials for luminescent labels. In recent years, there has been an increased interest in europium derivatives as candidates of biomedical markers.

Synthesis and experimental study of the luminescence of europium-containing compounds have been the subject of much research. At the same time, preference has always been for methods of investigation which enable the predetermined architecture of the material to be implemented in order to obtain a phosphor with the desired characteristics. The prediction of the emission properties of chromophores leads to fewer stages in exploratory chemical experiments and thereby to lower costs of research work. In this connection, the growing importance is attached to the theoretical prediction of the excitation spectra of new materials.

In [1–11], experimental studies of the Eu^{3+} luminescence were carried out, while theoretical studies are much less in number. In this respect europium complexes based on various ligands, e.g., cryptates, and crystalline, in particular nanocrystalline, inorganic matrices incorporating the Eu^{3+} ion were intensively studied theoretically.

An approach widely used for calculation of the theoretical luminescence spectra is based on the crystal field theory. Techniques for building the effective Hamiltonian of the crystal field theory for Eu^{3+} doped into various crystalline matrices were described for oxide (Gd_2O_3 [12], In_2O_3 [13], $Sr_{1-x}MoO_4$ [14], ThO_2 [15]), fluoride, and phosphate ($LiYF_4$, YPO_4) [16–17] matrices. The energy levels and theoretical luminescence spectra are calculated using empirical parameters. In some studies, theoretical ab initio calculations are combined with empirical calculations of the energy levels, e.g., for Ba_2LnMO_6 (Ln = Y, Gd; M = Nb, Ta) and $(Cs,Rb)_2(Na,Li)Eu(NO_2)_6$ [18, 19].

A similar approach was applied in [20] for a quantum-chemical study of the crystal field and determination of the charge transfer energy for nanocrystalline Y_2O_3. *Ab initio* methods were used for calculation of the ground-state ($4f^n$) energy and one-electron crystal-field parameters for Eu^{3+} in all the clusters simulating the local environment of Eu^{3+} in cubic Y_2O_3. For some levels the energies significantly differed from the experimental data. The best results were obtained for $(EuY_{12}O_{22})^{5-}$ cluster with 35 atoms.

Greater opportunities, compared to the crystal-field theory, are offered by the density functional theory (DFT) [21] which finds application in theoretical studies of the Eu^{3+} luminescence both in combination with empirical approaches [18–19] and independently [22–24]. In [22] the crystal-structure parameters for $Y_6W_xMo_{(1-x)}O_{12}$ were calculated, as well as the electronic structure and the orbital populations with the convergence of 1.0–1.6%. The calculations were performed for Y_6WO_{12} and Y_6MoO_{12} matrices, and this was followed by calculation of the excitation spectrum of the Eu^{3+} ion in the matrix. Local environment of Eu^{3+} in clusters was not considered in that study.

In [23], the DFT technique with the use of the supercell approach was applied to the calculation of the DOS diagram for Gd_2O_2S crystals. A DFT calculation of the absorption spectrum of Eu^{3+} for europium-doped aluminum nitride ($[EuAl_{12}N_4]^{26+}$ cluster) in [24] gave the results that showed only qualitative agreement with the experimental observations.

Among relevant theoretical studies, the all-electron calculation by the Hartree-Fock self-consistent field method of a system with an open shell configuration of the EuO_6^{9-} cluster in a Ba_2GdNbO_6 crystal [25] is worth mentioning.

One of the most promising methods that is currently used for estimating the excitation energies is the time-dependent perturbation theory (TD DFT). To the best of our knowledge, the only instance of application of this theory to Eu^{3+} luminescence calculations was in the case organic complexes of europium [26]. As to inorganic compounds, the TD DFT calculation of the electronic spectra of $CoZr_4 \cdot (PO_4)_6$ with application of a cluster approach was carried out in [27]. Thus, the calculations of the luminescence spectra are mostly performed by empirical approaches, crystal-field theory, while quantum-chemical calculations using DFT, in particular, TD DFT, methods are scarce. The extent of quantitative agreement between the theory and experiment is hardly discussed in those studies; the clusters selected not always adequately represent the local environment in the crystalline matrix.

This study was concerned with a Nasicon-structured europium-containing zirconium phosphate $Eu_{0.33}Zr_2(PO_4)_3$. Compounds of this structural type are well-known for their high cationic conductivity, radiation resistance, chemical and thermal stability [28]. Their most interesting feature is a high isomorphic capacity and the respective possibility of adjustment of properties [29]. Cationic substitutions in certain framework sites can produce changes in the photoluminescence characteristics of these compounds [30].

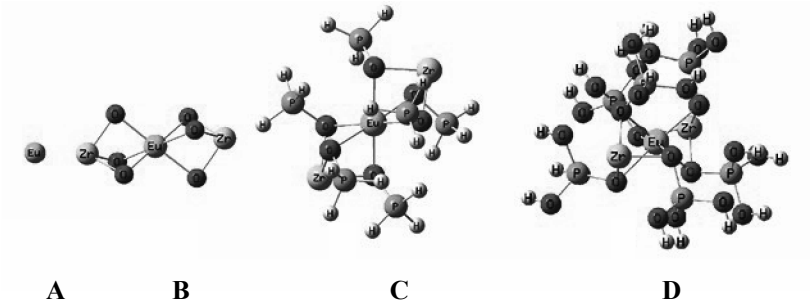
Here, we explored the possibility of theoretically predicting the Eu^{3+} luminescence in a Nasicon-structured inorganic crystalline matrix using the TD DFT method. Our purpose was to determine the coordination sphere to which we could restrict ourselves when selecting the cluster model. To this end, we carried out calculations for clusters of different size in which either the oxygen environment only (the first coordination sphere) or also the phosphate tetrahedra (the second and third coordination spheres) were taken into account.

When studying the emission properties of $Eu_{0.33}Zr_2 \cdot (PO_4)_3$ orthophosphate in which the Eu^{3+} ion is in the singlet state we used several approximations.

As the first approximation in the calculation of the excitation spectra all the cluster model components were treated as ions on the assumption that the Eu^{3+} ion will give a certain electrostatic contribution and that the nearest local environment corresponds to the ionic crystal lattice structure [31].

The second approximation consisted in passivation of the broken bonds by hydrogen atoms. Otherwise broken bonds will lead to a cluster whose properties will differ in multiplicity from the real system and thereby introduce distortion of the desired geometry and all properties of interest. However, bond passivation by hydrogen atoms also may affect the electronic state in the cluster and distort its wave function. Hence, there is necessary to choose such cluster model that the distortion will be minimized [32]. The optimal cluster is that having the smallest size though most accurately describing the desired properties. There exist two methods to construct clusters. In the first method, a smaller crystal system is cut out from a larger crystal system and then used in quantum-chemical modeling of luminescence. However, in this approach the choice of the smaller system is controversial. Therefore, we used the second method, in which the cluster is generated sequentially by building up the nearest environment around the emission center (Alexandrowicz method) [33].

The excited state calculations were carried out in the framework of the time-dependent density functional theory. The suitable functionals and potentials



A **B** **C** **D**

Europium ion (**A**) and clusters (**B**, **C**, and **D**).

were sought to provide agreement between the calculated and experimental wavelengths. This procedure is possible because the europium ion exhibits bands of two types, where the first type bands can change under the influence of the ligand field, and the second type bands always remain unchanged [34, 35].

Next, we proceeded to building up the nearest environment around the emission center. As new atoms (O, P, Zr) were incorporated into the cluster, new basis sets were added for each type of atoms, so that the necessary set of potentials could be obtained. The results of each calculation run were compared with the experimental data, and the calculation-comparison-adjustment procedure was continued until the calculated data agreed with the experimental results within 1%.

After the calculations using a number of functionals and basis sets were performed, we selected the parameters that yielded a numerically computed best fit with the experiment. Here, we did not perform assignment of wavelengths based on spectral terms. We selected B1LYP, B3LYP, and PBE0 functionals and MWB52, MWB53, MHF52, MHF53 pseudopotential basis sets for each of them.

The best agreement with the experimental data was achieved for B1LYP functional with MHF52 and MWB52 basis sets and for PBE0 functional with MWB52 basis set (Table 1). The use of B1LYP functional leads to fairly good results, but with PBE0 functional the computational time is 1.5 times smaller. Therefore, we chose the PBE0/MWB52 pair. To make the cluster geometry optimization faster we applied the molecular mechanics approach with the *universal force field* (UFF) potential [42, 43]. The figure shows how successively larger clusters were generated until adequate description of the emission properties of the crystalline compound under study was achieved.

By gradual transition from the smallest to a larger cluster after each procedure of sequential addition of atoms and optimization of the cluster model we performed calculations of the luminescent properties in the framework of the TD DFT theory using a combined basis set [44–46].

With the view of accelerating the calculation, as new types of atoms were incorporated into the system, we applied for each element a new basis set so that each system had its own basis set. For example, for lighter atoms we used simple basis sets, which allowed faster calculation and more flexible representation of the features of the structure calculated. It should be noted that the system growth in size is accompanied by

Table 1. Wavelengths calculated by the TD DFT method with different functionals and basis sets for Eu^{3+}

Functional	Basis set	Wavelength, nm
B1LYP	MHF52	373, 525
	MHF53	288
	MWB52	404, 459
	MWB53	306
B3LYP	MHF52	488
	MHF53	254
	MWB52	576
	MWB53	268
PBE0	MHF52	370, 516
	MHF53	284
	MWB52	400, 453
	MWB53	307
Experiment		270, 297, 304, 375, 393, 415, 465, 525, 577

Table 2. Luminescence wavelengths, nm

Calculation			Experiment [48]
B	**C**	**D**	
1753.8	838.2	462.1	462.9
1582.6[a]	788.5	430.9	441.9
1510.1	768.0	424.0	412.9
1509.4	728.3	414. 6	400.0
1360.5[a]	699.8	389.8	391.9
1293.3	677.0	379.4	380.7
1291.8	634.1	375.5	–
1285.4	594.0	371.5	–
1236.6[a]	584.6	357.7	361.3

[a] Zero intensity.

Table 3. Average experimental and average calculated bond lengths, nm

Bond	Experiment [49]	Calculation	Deviation, %
Eu–O	0.260	0.230	–11.5
Zr–O	0.203	0.212	4.4
P–O	0.149	0.169	13.4

conjugation of the outer shells of atoms with those of other atoms, and the electron density is redistributed on the atomic orbitals, in particular, on the emitting center. Therefore, we introduced a correction to the pseudopotential, allowing the occurrence of interaction of all molecular orbitals [47].

The number of electrons in the cluster should correspond to that in the analogous segment of $Eu_{0.33}Zr_2(PO_4)_3$ orthophosphate, and so we assigned formal charges to the clusters using the ionic bonding model.

We calculated the excitation spectra of $[EuZr_2O_6]^{-1}$ (**B**), $[EuZr_2P_3O_6H_6]^{+11}$ (**C**), and $[EuZr_2P_6O_{24}H_{18}]^{+11}$ (**D**) clusters and compared the results with the experimental data (Table 2). As the cluster was built up sequentially, the spectrum underwent significant changes. The optimal cluster is $[EuZr_2P_6O_{24}H_{18}]^{+11}$ with 51 atoms, providing the most adequate description of the luminescent properties observed.

The reason for a slight deviation of the calculated from experimental data is most likely twofold: a well-chosen pseudopotential for the emitting center and a well-chosen force field such that the global or near-global energy minimum was achieved. This, in turn, allowed obtaining the optimal geometry for the cluster corresponding to the Nasicon-type crystal structure under study (Table 3).

Unfortunately we did not have sufficient computing power for calculating the optimal geometry in the framework of the DFT theory. However, considering the emission features of the central atom as the focus of our study, we proceeded from the fact that it is only affected by the field of the neighbor atoms. A good agreement between the experimental and theoretical results is indicative of good performance of the truncated model, cluster D, which takes into account not only the nearest-neighbor oxygen atoms but also the phosphate groups and in which the broken Zr–O bonds are passivated by hydrogen atoms.

Thus, we demonstrated the real possibility of a quantum-chemical calculation of the luminescent properties of Eu^{3+} in a Nasicon-type matrix using the cluster model. The algorithm found can be applied to other compounds, which opens prospects for predicting the luminescent properties of new materials and allows determining the range of potential emitters.

The calculations were performed using the GAUSSIAN 03 program [50].

ACKNOWLEDGMENTS

The authors are grateful to S.V. Zelentsov and S.K. Ignatov for the participation in discussion of the results.

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