

**DETERMINATION OF THE POSITION OF A DOPANT BY DFT ANALYSIS;
SOLID-STATE SYNTHESSES OF $Zn_3Nb_2O_8$ DOPED WITH Eu^{3+}**

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Abstract

The present paper aims to provide an objective criterion for establishing the position of a dopant (Eu^{3+}) in a given crystalline matrix ($Zn_3Nb_2O_8$). Following the analysis of the general conditions, regarding the size of the doping ion correlated with the reticular distances and / or the size of the coordination polyhedra, it remains to be established the concrete place that it will occupy, substitutional or interstitial. The criterion is based on the principle of minimum energy of the system, as a condition of existence of doped structure, which is why the method is applicable for a large variety of crystalline materials.

Introduction

The design of the properties of a material is increasingly used, as a step prior to its synthesis. The most effective and direct method of modulating the properties of a material with a crystalline structure is to use a certain dopant. All its physicochemical properties are strongly influenced both by the nature and concentration of the dopant and by its position in the host crystal lattice. The development of computing power in the last 3 decades has made possible the emergence of a wide range of software used in materials design, as direct applications of *ab-initio* computational methods of quantum chemistry. DFT is one of these methods, which has gradually become a practical tool in engineering and modeling the properties of crystalline materials. As will be seen in this paper, the efficiency of the method is inextricably linked to the computing power available and inherently correlated with the complexity of the crystal structure analyzed. The convergence of the energy of a crystalline system towards a minimum value in order to achieve a state of stability is the fundamental criterion by which its existence is found. For calculating the energy of crystalline materials, DFT is an increasingly widely used method, providing a good correlation with experimentally determined values. At the outset, it should be emphasized the seemingly paradoxical fact that the calculation difficulties are greater the lower the level of doping. Also, the application of the method is simpler in the substitutional case than in the interstitial case. [3]

Figure 1 shows the elementary cell of $Zn_3Nb_2O_8$ in which 26 ions are identified: 4 Nb, 6 Zn and 16 O with their 300 electrons. In order to refer to low-concentration doping, the elementary cell would have to be multiplied a certain number of times, thus obtaining a supercell. Only in the supercell can we speak of introducing an impurity element at a low concentration in relation to the host ions. The smallest supercell that complies with the spatial symmetry conditions corresponding to the space group C2/c (No. 15) to which $Zn_3Nb_2O_8$ belongs contains 208 ions and a proportionally higher number of electrons, which makes the calculation unfeasible, assuming logistics that far exceed any justification for the case under consideration. However, *ante-factum*, it is possible to determine the place that the doping ion can occupy within the elementary cell, even in this case.

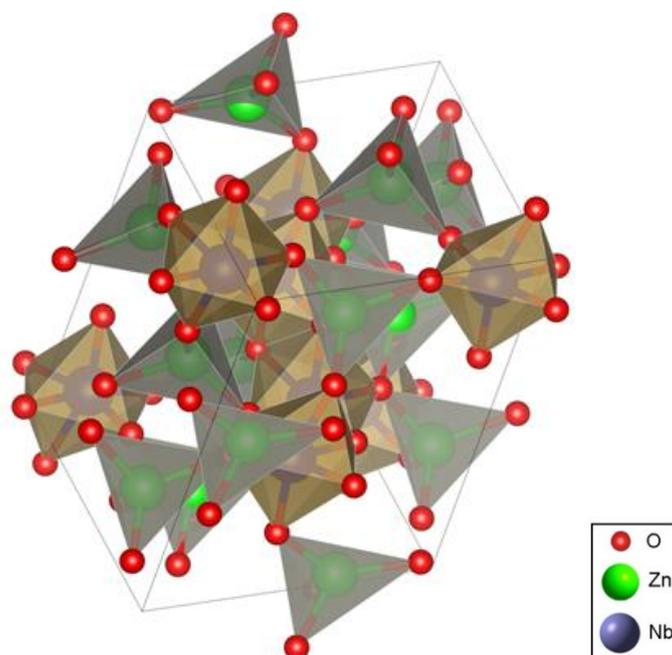


Figure 1. Elementary cell of $\text{Zn}_3\text{Nb}_2\text{O}_8$ obtained by CRYSTAL 14 package

Results and Discussions

Note the coordination polyhedra of Nb and Zn. In the case of Zn we notice two distinct positions, irreducible from a symmetrical point of view, denoted by Zn1 and Zn2 respectively. We will be interested in what substitute positions are eligible for the Eu ion and whether interstitial positions are possible. The fact that the Eu ion originating from Eu_2O_3 is octahedrally coordinated allows us to assume that it can substitute Nb ions within the host network, also octahedrally coordinated. Here, however, begins another type of problem regarding the use of the software. The information it needs to build the elementary cell in the lattice refers to the symmetrically irreducible positions – the asymmetric unit after which it is necessary to communicate to it the group of spatial symmetry with which it must operate. Since in the asymmetric unit there is only one Nb ion, after the reconstitution of the entire elementary cell, all Nb atoms will be replaced by Eu! Basically, we are no longer talking about $\text{Zn}_3\text{Nb}_2\text{O}_8$ but about the structurally equivalent network $\text{Zn}_3\text{Eu}_2\text{O}_8$. The calculation of DFT converges towards a minimum energy, so this material possesses a thermodynamically stable structure. In conclusion, it is permissible for Eu to substitute for Nb. Because, for example, its forbidden band calculated for $\text{Zn}_3\text{Eu}_2\text{O}_8$ is 2.5 eV, much smaller than the original compound's forbidden band of 3.7 eV [1], it is obvious that it will narrow after doping. Testing other substitution positions for both Zn1 and Zn2, similar substitution calculations reveal convergence towards energy minimums in both cases. The synthesis process allows the reaction to take place competitively between Eu and Zn ions, not successively; does not occur the initial formation of the $\text{Zn}_3\text{Nb}_2\text{O}_8$ crystal matrix, after which the Eu^{3+} dislodge the Zn ions in the two positions. On the contrary, Eu with more available electrons in valence layers than Zn, is more reactive, will occupy the places in the network before Zn. In these cases, in which it is practically not a doping but a massive impurification, resulting in a compound of the type $\text{Zn}_{3-x}\text{Eu}_x\text{Nb}_2\text{O}_8$, the calculation of the band structure reveals the cancellation of the band gap, the material becoming conductor, fact due to a much more number large of weaker electrons tied in the Eu, which easily become mobile in the network. At the same time, Eu ionic radius $R = 0,947\text{\AA}$ can find a place and interstitial, conserving the spatial symmetry.

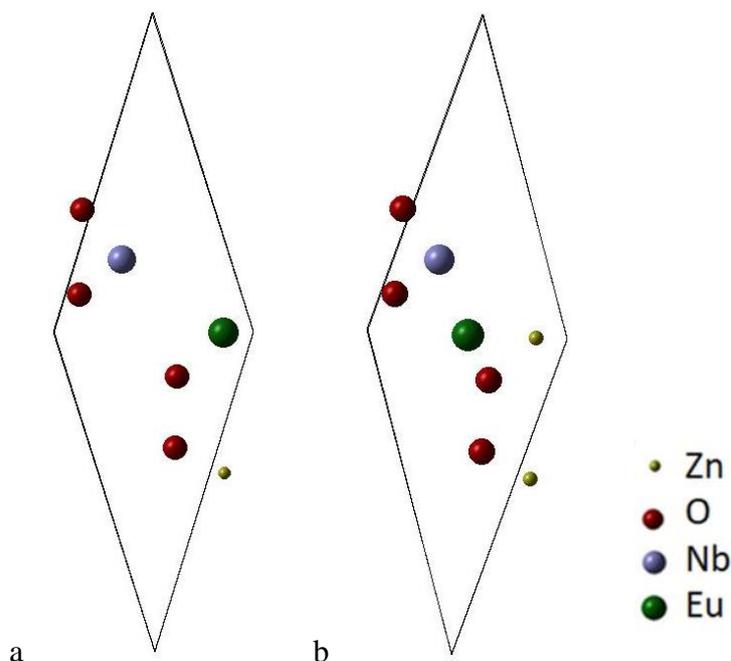
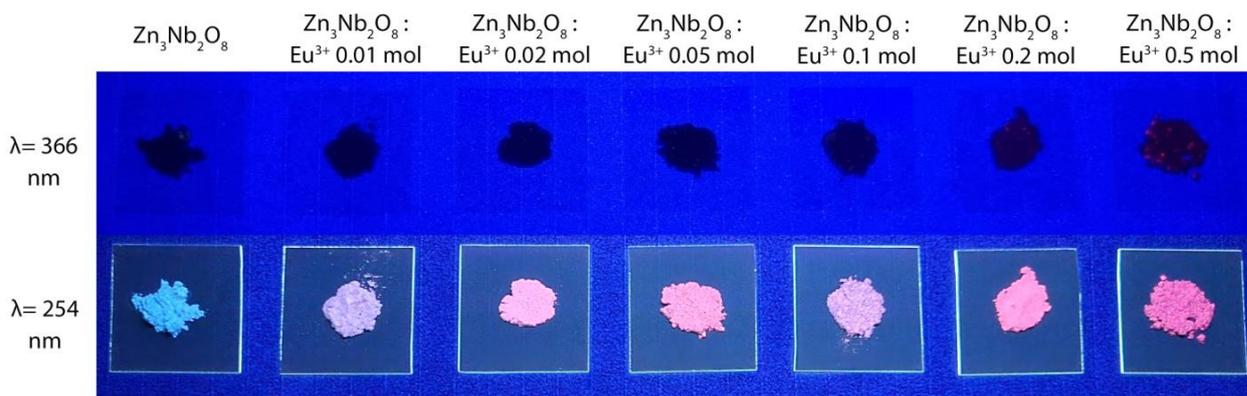


Figure 2 a. Eu³⁺ substitutes Zn b. Eu³⁺ - interstitial position

The calculation of DFT in the case of the figure above, with Eu ions placed median in the elementary cell, was not completed by convergence due to mutual influence in between. This inconvenience is canceled in the case of low concentrations, specific to doping. As an experimental study, a series of samples of Zn₃Nb₂O₈ doped with Eu³⁺ at various concentrations were obtained by solid-state thermal synthesis. The precursors used were niobium pentoxide Nb₂O₅ (99.9%), zinc oxide ZnO (99.9%) in molar ratio 3:1 to which europium (III) oxide Eu₂O₃ (99.9%) was added in concentrations 0.01%, 0.02%, 0.05%, 0.1%, 0.2% and 0.5% respectively. [1]



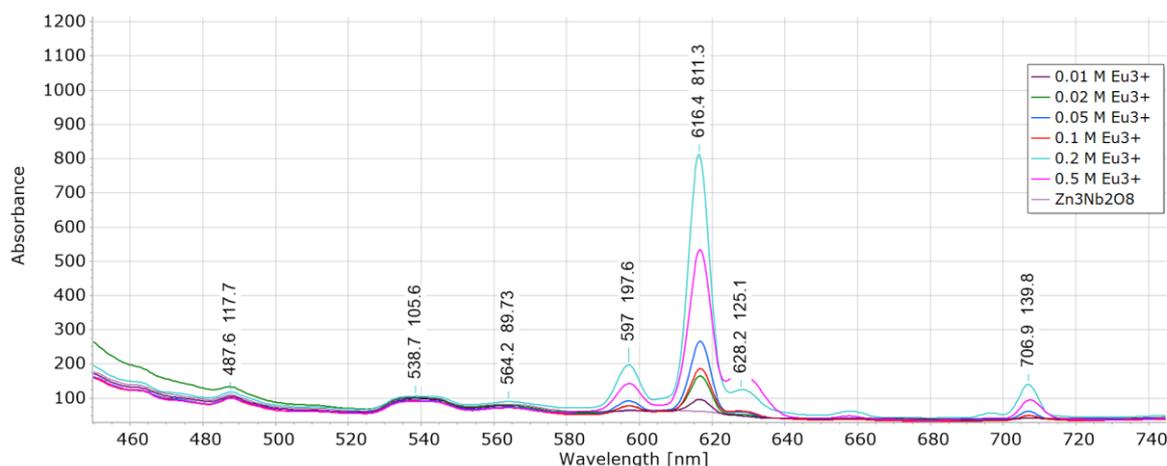


Figure 3. Samples and UV-VIS spectra for Eu^{3+} -doped $\text{Zn}_3\text{Nb}_2\text{O}_8$ at these concentrations.

Conclusion

The DFT method used in CRYSTAL 14 software offers the possibility to determine the position of a dopant in a given crystal matrix. Its advantage lies in its general and objective character, overcoming the difficulties that arise in the case of dopants that do not bring significant changes in the crystal lattice, preserving its symmetry. Experimental arguments, of which the diffraction spectrum XRD being the most important, encounter some inherent difficulties for the following reasons. In the case of interstitial doping, in principle, some additional picks occur due to the appearance of new crystalline diffraction planes in the host matrix and some displacement of some of them due to cross-linking changes. In the case of substitutional doping, where no additional plans appear in the network, no additional picks occur, because only the distance between plans can be modified; some picks move one way or the other, as distances between planes decrease or increase. But these effects depend decisively on the concentration of the dopant and its ionic size.

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References

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