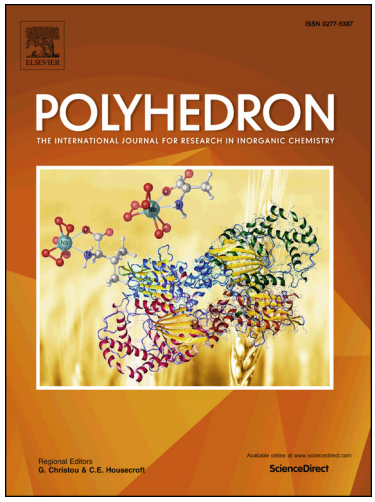

Temperature and pressure dependence of local structural changes around Gd^{3+} centers in $RAl_3(BO_3)_4$ crystals: Modeling zero-field splitting parameters

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Temperature and pressure dependence of local structural changes around Gd^{3+} centers in $RAl_3(BO_3)_4$ crystals: Modeling zero-field splitting parameters

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Abstract
The semi-empirical superposition model (SPM) analysis is applied to predict the zero-field splitting parameters (ZFSPs) of Gd^{3+} ions doped into $RM_3(BO_3)_4$ (RAB) as well as the structural changes around these paramagnetic centers located at possible cation sites in these crystals. Theoretical investigations are aimed at explanation of the temperature dependence of the local structural parameters of Gd^{3+}:RAB (R = Y, Eu, Tm). The results of spin Hamiltonian (SH) analysis of electron magnetic resonance (EMR; EPR - electron paramagnetic resonance) spectra serve for fine-tuning the theoretically predicted zero-field splitting (ZFS) parameters (ZFSPs) obtained using SPM. This approach enables determination of the local structure changes around Gd^{3+} centers in RAB crystals and explains the observed temperature dependence of the ZFSPs. For Gd^{3+}:EuAB, due to availability of the data, also the observed pressure dependence of the ZFSPs is considered. For this purpose, the distortions parameters, i.e. the changes in the ligand's distances ΔR_i and the angular distortions $\Delta\theta_i$, have been treated as variable parameters in SPM analysis. This procedure yields good matching of the calculated ZFSPs and the experimental ones, and enables determination of the corresponding local distortions. The present results may be useful in future studies aimed at technological applications of the Huntite-type borates with the formula $RM_3(BO_3)_4$. The model parameters determined here may be utilized for ZFSP calculations for Gd^{3+} ions at octahedral sites in single-molecule magnets and single-chain magnets.

Keywords: Electron magnetic resonance (EMR); Zero-field splitting; Temperature and pressure dependence; Gd^{3+} ions in $RAl_3(BO_3)_4$ (RAB, R = Eu, Y, Tm).

1.Introduction

In recent years, there has been a growing interest in the borates crystals as very useful materials due to their distinctive optical properties and, especially, in view of potential applications in tunable lasers. These compounds are represented by the formula $RM_3(BO_3)_4$ (RMB), where R is the trivalent rare-earth (RE) ions and M = Al, Sc, Fe, Cr, Ga. Doping these materials with paramagnetic ions (namely, RE (4f) and transition metal (TM) (3d) ions) provides means to enhance their optical properties and achieve suitable magnetic properties. It was proven that borates having non-centrosymmetric sites are excellent host matrices for substitution of RE ions. Hence, many studies have reported crystal growth and spectroscopic characteristics of $RM_3(BO_3)_4$ systems doped with various RE ions (e.g., Gd^{3+}, Nd^{3+}, Tb^{3+}, Sm^{3+}, Ce^{3+}) [1,2,3,4,5,6]. By the substitution of RE ions into borates their optical and magnetic properties can be easily tuned. Knowledge of the effects of the dopants ions on the structural, magnetic, and electrical properties of host materials is crucially important to tune these crystals for better technological applications. Hence the factors like the actual cation substitution sites and the local structural distortions induced by dopant ions must be well understood. EMR (EPR) studies [7,8,9,10] are very useful in this regard.

The first EMR investigation [7-10] of Gd^{3+} doped YAB [11] has enabled determination of the magnitudes and signs of the spin Hamiltonian (SH) parameters; for review of the SH notations, see, e.g. [12,13,14]. Subsequently, the temperature and pressure dependence of EMR spectra for Gd^{3+} ions in EuAB were reported [15] as well as the second-rank axial zero-field splitting (ZFS) parameter (ZFSP) b_2^0 [12-14] was analyzed theoretically using the semi-empirical superposition model (SPM) [16,17]. Most recently the Gd^{3+} centers in three RAB crystals (EuAB, YAB, and TmAB) were studied [18] and the results were