ESR AND LUMINESCENT STUDY, *AB INITIO* MODELLING OF ATOMIC AND ELECTRONIC STRUCTURE OF NATURAL CARBONATE MINERALS $(Ca,Mg)CO_3:Mn^{2+}$

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The scheme of calcite and dolomite classification based on the data of ESR, thermo- and X-ray luminescense (in the temperature range 77-400 K) of the typical impurity Mn^{2+}-ions replacing Ca^{2+} (Mg^{2+})-ions in carbonates is under consideration. The scheme is based on the statistical analysis of more than 1000 carbonate samples of different Mn^{2+} content, genesis and age (from Riphean up to the modern sediments). Numerical ESR and luminescense databases have been created. It has been shown that under the temperature changes analytical spectroscopic Mn^{2+} line widths, their intensities and their dynamics varied essentially in the samples and depended on the minerals content, their structure defectness and genesis. Suggested scheme of carbonates classification has been used for the analysis of stromatolite-containing limestones, dolomites and interstromatolithic layers from all main South Urals Riphean formations series and some Riphean carbonates from other Russian and world regions. The experimental spectroscopic data have been analyzed using the results of theoretical modelling for calcite and dolomite. The atomic and electronic structures of the minerals were simulated by *ab initio* quantum-chemical cluster methods in terms of GAMESS and X_α-DVM codes on the base of the multiprocessing computer system MVS-1000 of the Institute of Mathematics and Mechanics UrB of RAS (Ekaterinburg). For investigation of pure calcite we used 53-atomic $[Ca_{cent}Ca_6C_6O_{42}]^{46-}$ and 64-atomic $[C_{cent}C_{12}Ca_6O_{45}]^{26-}$ clusters containing the central octahedron $Ca_{cent}O_6$ and the central CO_3-group, respectively. For investigation of dolomite we used 71-atomic $[Ca_{cent}Ca_4Mg_6C_6O_{54}]^{62-}$, $[Mg_{cent}Mg_4Ca_6C_6O_{54}]^{62-}$ and 49-atomic $[C_{cent}C_6Mg_3Ca_6O_{36}]^{32-}$ clusters corresponding to its structure. The isomorphic substitutions of Ca (Mg) by Mn, Sr, Fe, Mg, Ca-ions have been analyzed as well. The relaxed structure of the clusters with the impurities was determined by the total-energy minimization using the GAMESS software. Using the spatial integrating of the electron density in the clusters the effective charges of atoms have been calculated. Taking into account the peculiarities of spatial distribution of the total and deformation electronic density in the clusters the high covalency within the CO_3-groups has been revealed. The variations of the spectroscopic properties of the Mn impurity ion in calcites and dolomites of the different geneses have been explained due to the variations of settlement values of Mn effective charge, the ionicity degree and Mn-O length in MnO_6 octahedrons.

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