

Optical spectra of Co^{2+} in three synthetic silicate minerals

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ABSTRACT

Polarized optical absorption spectra of three synthetic Co-bearing silicates, orthopyroxene, olivine and beryl, were studied at room and liquid nitrogen temperatures. In all three matrices, Co enters octahedral structural sites as the Co^{2+} ion. In accordance with the d^7 electronic energy level diagram, the spectra show three distinct band systems which are assumed to originate from three spin-allowed dd transitions of Co^{2+} , ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{2g}({}^4F)$, ${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F)$, and ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$. The number of bands is different in different matrices and is regulated by the splitting of electronic states, symmetry selection rules for electronic transitions between them, and Co^{2+} ion distribution between non-equivalent structural sites. Due to a strong preference of Co^{2+} for the M2 site and the greater intensities (oscillator strengths) of electronic dd transitions for Co^{2+} in the M2 site, M2 Co^{2+} bands prevail in the $(\text{Mg},\text{Co})\text{SiO}_3$ orthopyroxene spectra. In olivines, the number of bands is larger than in orthopyroxene due to the combined contribution of both M1 Co^{2+} and M2 Co^{2+} ions. By comparison of the $(\text{Mg},\text{Co})_2\text{SiO}_4$ and Co_2SiO_4 olivine spectra, the bands caused by M1 Co^{2+} and M2 Co^{2+} were distinguished. The spectra of Co-bearing beryls, $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$, prepared by both flux and hydrothermal growth, indicate that Co enters the structure mostly as Co^{2+} in the octahedral Al-site.