

Optical absorption spectroscopy of transition metal ions-bearing minerals at different temperatures and pressures: some crystal chemical and thermodynamic aspects

Michail Taran

Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Science of Ukraine, Kyiv, Ukraine

There are at least three most important aspects of optical absorption spectroscopy of transition metal ions ($3d^N$ -ions) in minerals at different temperatures (T) and pressures (P). *First*, this significantly contributes to interpretation of mineral spectra. Since absorption bands caused by electronic transitions within partly filled electronic d -shell (dd -bands) or between structurally adjacent transition metal ions of variable valences (intervalence charge-transfer transition or IVCT bands, usually of $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$ or $\text{Fe}^{2+} + \text{Ti}^{3+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$ type) have different nature, their reactions on T and P are essentially different and, therefore, can be used for their recognition and interpretation of the absorption spectra. Besides, there are distinct differences in T- and P-dependencies of the homonuclear and heteronuclear IVCTs, as well as between dd -bands of $3d^N$ -ions in different coordination, symmetry of the ligand surrounding, exchange coupled interaction and other effects which can also be helpful at interpretation of the spectra. *Second*, since transition metal ions constitute almost 48 wt. % of the Earth and due to specific features of their electronic configuration they significantly influence thermal, electric, magnetic and other physical properties of minerals and rocks. Therefore, optical spectroscopic investigation of $3d^N$ -ions-bearing minerals at high T and P give important information on mineral properties in Earth depths. For instance, elastic constants of minerals are the key to understanding geophysical properties of the Earth's interior. Bulk moduli of $3d^N$ -ion-centered coordination polyhedra, which can be derived from pressure-induced variations of optical absorption spectra, influence the velocities of seismic waves used for determination of the internal structure of the Earth. Also, radiative thermal conductivity of the Earth's mantle and transition zone can be evaluated from infrared and optical absorption spectra of $3d^N$ -ion-bearing minerals which depend on T and P. *Third*, T and P influence on such specific characteristic of $3d^N$ -ions as crystal field stabilization energy (CFSE). This may have a measurable effect on inter- and intracrystalline partition of transition metal ions in the Mantle conditions. Particularly, in case of Cr^{3+} which has the highest CFSE in octahedral coordination among all other $3d^N$ -ions, P- and T-parameters may influence the contribution of CFSE to the mixing enthalpy of Cr^{3+} -containing solid solutions and, thus, may be the cause of increased concentration of chromium in many deep seated solid phases as pyropes, spinels, corundums, clinopyroxenes, olivines etc. On the other hand, effects of T and P on Racah parameter B evidence that in depths, at high PT-conditions, ionic character of chemical bond between $3d^N$ -ions and oxygen is predominating. Therefore, the character of $3d^N$ -ion- O^{2-} -bond hardly strongly influences intercrystalline distribution of $3d^N$ -ion in the Earth depths.