Structural relaxation around Co^{2+} in synthetic blue $(Mg,Co)Al_2O_4$spinelcrystals

G.B. Andreozzi[1], V. D'Ippolito[1], F. Bosi[1] and U. Halenius[2]
[1]Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro5, 00185 Roma, Italy
[2]Department of Mineralogy, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden

Co-bearing spinel crystals are rare in nature and actively sought as gemstonesbecause of their vivid blue color, while synthetic Co-spinel powders are largely used as ceramic pigments. In the present work, single crystals belonging to spinel s.s. ($MgAl_2O_4$) - cobalt spinel ($CoAl_2O_4$) series were synthesized by flux growth method with $Na_2B_4O_7$ as flux.Low cooling rates (2°C/h) and linear temperature profiles were applied in the thermal interval 1200-800°C.Thermal runs were performed in reducing atmosphere (10^{-8} - 10^{-15}bars) created by a continuous flow of CO_2/H_2 with a ratio of 100/4 cm^3/min. With increasing Co contents, the crystals varied in colour from light blue to intensely dark blue. Selected crystals were investigated by electron-microanalysis,single-crystal X-ray diffraction and UV-VIS-NIR-MIR spectroscopy to obtain the actual chemical composition,structural characterization, cation site population and quantitative optical absorption. The crystals are chemically homogeneous, with composition dominated by the $Co^{2+} \rightarrow$ Mg substitution and structural parameters *a*, *u*regularly increasing with Co^{2+}.Along the series, Co^{2+} shows a marked preference for the tetrahedral coordination with respect to Mg. The optical absorption spectra, measured between 4000 and 35000 cm^{-1}, exhibit three spin-allowed electronic *d-d* transitionsat ~17000, ~8000 and ~4500 cm^{-1}, attributed tothe tetrahedrally coordinated Co^{2+}. Because no absorption bands related to either octahedrally coordinatedCo^{2+} or tetrahedrally/octahedrally coordinated $Co^{3+}$are observed,the recognized increase of absorption of the spin-allowed Co^{2+}*d-d* bands with increasing Co-content indirectly causes the colour change from light blue to intensely dark blue.The energy of the absorption band at ~ 4.500 cm^{-1} is directly proportional to the crystal field, and 10 *Dq* values are directly related to the bond distance, indicating that in the $MgAl_2O_4$–$CoAl_2O_4$ solid solution series the local arrangement of atoms around Co^{2+} is almost fully relaxed.