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Blue spinel crystals in the $MgAl_2O_4$-$CoAl_2O_4$ series: Part I. Flux growth and chemical characterization

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Abstract

Natural blue Co-bearing spinel crystals are rare and actively sought as gemstones, while synthetic blue Co-bearing spinel powders are largely used as ceramic pigments. High-quality spinel single crystals with compositions closely corresponding to the solid-solution series spinel sensu stricto ($MgAl_2O_4$)-cobalt spinel ($CoAl_2O_4$) were produced 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, followed by rapid cooling. Thermal runs were performed in reducing atmosphere (f_{O_2} 10^{-8}–10^{-15} bars) created by a continuous flow of a CO_2:H_2 mix with a ratio of 100:4 (cm^3/min). Ten experiments were successfully carried out and hundreds of inclusion-free gem-quality single crystals (up to 1 mm large) were produced in each of them, sometimes together with crusty aggregates and microcrystalline powder. Selected crystals were investigated by SEM/EDS X-ray mapping to check for compositional homogeneity and by electron-microprobe analysis to obtain the chemical formula. Crystals were found to be chemically homogeneous and entirely representing the $MgAl_2O_4$-$CoAl_2O_4$ solid-solution series, with the latter component ranging from 7 to 100%. With increasing Co^{2+} contents, the crystals vary in color from light blue to intensely dark blue in daylight. The unit-cell parameter *a* increases from 8.084 to 8.105 Å along the solid-solution series, and the observed increase is determined more by the inversion degree than by the variation in Co contents. The composition of crystal products does not correspond to the composition of the starting oxide mixture, being cobalt enriched in the crystals. A tentative explanation of this behavior is suggested by considering possible ionic potential as well crystal field stabilization effects.

Keywords: Cobalt spinel, $CoAl_2O_4$, single crystal, flux growth, electron microanalysis