Blue spinel crystals in the MgAl$_2$O$_4$-CoAl$_2$O$_4$ series: Part I. Flux growth and chemical characterization

VERONICA D’IPPOLITO,$^1$ GIOVANNI B. ANDREOZZI,$^1$* FERDINANDO BOSI,$^1$ and ULF HÅLENIUS$^2$

$^1$Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Roma, Italy
$^2$Department of Mineralogy, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden

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$_2$O$_4$)-cobalt spinel (CoAl$_2$O$_4$) were produced by flux growth method, with Na$_2$B$_4$O$_7$ 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 ($f_0_2$ 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$_2$O$_4$-CoAl$_2$O$_4$ 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$_2$O$_4$, single crystal, flux growth, electron microanalysis

INTRODUCTION

Co-bearing spinels are very rare in nature, but are actively sought as gemstones due to their vivid, high-purity blue color that makes them more precious than sapphires. Previous studies evidenced small amounts of cobalt (CoO = 1 wt%) in natural gems of Sri Lanka (Shigley and Stockton 1984) and in a sample from the island of Samos (Taran et al. 2009). Although the cobalt contents were very low, these natural Co-bearing spinel crystals showed light and fancy blue colors. Up to a few decades ago cobalt was considered a coloring agent only of synthetic blue spinel, whereas the blue color in natural spinel was attributed solely to iron. However, Shigley and Stockton (1984) demonstrated that both cobalt and iron are capable of producing blue colors in materials, and considerably less cobalt than iron is required to produce an equally intense blue. Besides the above mentioned natural Co-poor spinel crystals, the only reported natural occurrence of a Co-rich spinel (CoO $\leq$ 22.8 wt%) is a very small crystal (~200 µm large) included in a gem-quality blue sapphire from Bo Phloi, Thailand (reported as Bo Ploi in gemological literature), occurring in alluvial/eluvial deposits near basaltic outcrops (Guo et al. 1994).

Synthetic CoAl$_2$O$_4$ spinel is a high-temperature oxide (melting point of 1955 °C), and it is the most stable compound of a family of spinel-structured oxides obtained from Co$_2$O$_3$ at progressive increase of Al contents (Tielens et al. 2006, 2009). From an optical point of view, the increase of Al results in the transition from black Co$_2$O$_3$ to dark green Co$_2$Al$_2$O$_4$, bright blue Co$_5$Al$_2$O$_8$, and white Al$_8$O$_4$, that is, $\gamma$-Al$_2$O$_3$. These color changes are functions of both the oxidation states and the structural position of the cobalt cations. The black color is caused by total absorption of visible light due to the interactions between Co$^{2+}$ and Co$^{3+}$ (i.e., comparable to Fe$^{2+}$-Fe$^{3+}$ in magnetite), the dark green color is ascribed to electronic transitions in Co$^{3+}$ in octahedral coordination, and the bright blue color results from electronic transitions in Co$^{2+}$ in tetrahedral coordination (Burns 1993; Fernández and Pablo 2002; Tielens et al. 2006, 2009; Kurat et al. 2011). Bright blue synthetic CoAl$_2$O$_4$ is commercially well known as Thenard’s blue and has been extensively used, since the discovery of its industrial synthesis route in 1802, as a pigment (classified with the DCMA number 13-26-2) for the coloration of ceramics, glazes, porcelain enamels, glass, paint, fibers, paper, cement, rubber, plastics, and cosmetics. Cobalt-bearing pigments, commonly Co-spinel and Co-olivine, are the most efficient and widely used blue ceramic pigments, but the spinel is strongly preferred to olivine since a navy blue color can be obtained with strongly reduced CoO content (42 wt% in CoAl$_2$O$_4$ against 71 wt% in Co$_2$SiO$_4$), besides some differences