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**CHEMICAL AND OPTICAL STUDIES OF  
CORUNDUM MINERALS OF SRI LANKA**

A THESIS PRESENTED BY

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IN PARTIAL FULFILMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

**MASTER OF PHILOSOPHY**

OF THE

UNIVERSITY OF PERADENIYA

SRI LANKA

MAY 25, 1989

INORGANIC RESEARCH LABORATORY  
DEPARTMENT OF CHEMISTRY

**417813**

## ABSTRACT

The value of gemstones mainly depends on their attractive colour. Blue sapphire and ruby are the most common stones which occur in Sri Lanka. The origin of colour in gemstones is attributed to some transition metal ions, present in their crystal lattice instead of Al ions. These substituted cations themselves are coloured by absorbing certain wave lengths in the electromagnetic spectrum. However, the phenomenon of colour is not totally understood, except in few cases such as the red colour in ruby which is due to the crystal field absorption of  $\text{Cr}^{3+}$  ions. The contents in this thesis, mainly cover the chemical nature and the colour of corundum types of minerals.

The collection of samples have been carried out in major gem areas near Ratnapura and Elahera. Gemstones which are free from inclusions were selected and the chemical nature was studied by chemical analyses. Physical studies were carried out by X-ray powder diffraction, UV-VIS-near IR spectroscopy and Mössbauer spectroscopy. Apart from these natural gems synthetically produced Verneuil blue sapphire was also studied by above methods. The effect of heat treatment on the optical properties of corundums were studied.

It was found that the differences of cell parameters in natural and synthetic corundum become higher with respect to their cationic radii. But these differences in heat treated crystals were not observed under the experimental conditions, though the colour has changed. Observed compositional variations indicate that the important substitutions are Cr in ruby, Fe/Ti in blue sapphires and iron mainly in blue and yellow coloured sapphires. The low content of iron present in the crystal lattice is insufficient to provide a well-resolved M $\ddot{o}$ ssbauer spectrum of natural corundums.

The optical absorption patterns have shown different types of transitions such as crystal field, exchange coupled and charge transfer transitions. Transitions of Cr<sup>3+</sup> in ruby are a strong evidence for the crystal field transitions. The low proxying of trivalent iron in yellow sapphire is not sufficient to produce single ion transition. It was suggested that the yellow colour of sapphire arises from both single ion and exchange coupled pairs of Fe<sup>3+</sup> - Fe<sup>3+</sup> ions. The high intense broad band in blue sapphire has been sorted out as charge transfer process between Fe and Ti ions. The relative energies and band intensities of these types of transition depends on the site symmetry, heat treatment, composition and polarization. Chapter three describes the differentiation of these transitions. Except the charge transfer

bands there were low intensity spin forbidden absorption bands due to  $\text{Fe}^{3+}$  ion in UV region. It was realized that the blue colour of sapphire arises not only due to Fe/Ti charge transfer process but also due to spin forbidden single and exchange coupled pair of  $\text{Fe}^{3+}$  ions.

The enhancement of colour has been done at different environmental conditions. It was found that the heating should be performed under controlled oxygen pressure conditions to control the oxidation degree of Fe and Ti metal ions.

In addition, the colour of corundum comes from the electronic interaction of foreign atoms present in the crystal lattice. Although, the colour intensity is governed by their concentrations, types of interactions cationic positions and polarization. Cr (III) in corundum appears as red in colour due to its crystal field interaction. Exchange coupled pair and crystal field transitions of Fe (III) at first and second nearest neighbour site of the trigonal octahedra, give the yellow colour in yellow sapphire. The charge transfer process between Fe and Ti at first and second nearest neighbour site give the blue colour. Though the content of Fe and Ti is very low, it gives very attractive blue colour because of the charge transfer interaction (after Ferguson and Fielding 1972).

Enhancement of colour by heat treatment should be carried out under slightly reduced environment while protecting the effective oxidation degree of substituted cations.

