CHEMICAL AND OPTICAL STUDIES OF SPINEL GROUP OF MINERALS OF SRI LANKA

A THESIS PRESENTED

BY

CHANDANA PREMAKUMARA UDAWATTE

IN PARTIAL FULFILMENT OF THE REQUIREMENTS

FOR THE AWARD OF

MASTER OF PHILOSOPY

IN THE

UNIVERSITY OF PERADENIYA

SRI LANKA

AUGUST 1991

INORGANIC RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY

Abstract

Spinel group of minerals has a wide geologic distribution as accessory minerals and possesses the general formula AB_2O_4 in which A is usually a divalent cation. The order-disorder phenomena in $MgAl_2O_4$ spinel were studied by using ^{27}Al-NMR spectroscopy and X-ray powder diffractometer.

The natural spinel sample studied in this study shows a high degree of ordered cation distribution, while the synthetic samples are substantially disordered with a degree of inversion (X) of 0.45. The results also indicate, an increase in disorder with resing temperature with X going from 0 to 0.33 at 1000^0C for the natural spinel.

The colour is also a very important property of spinel. spinel investigated cation 69.5-71.0 wt% Al_2O_3 and 27.0-28.0 wt% MgO except in samples in which high FeO and ZnO contents were present. All coloured samples were found to contain transition metals such as Mn, Fe, Co, Ni, Ti, V, and Cr in varying amounts which are responsible for the colours exhibited by this mineral. Among these iron is the predominant element and its concentration was found to be in the range of 0.5-1.8 % by weight. The relative abundance of these ions can be approximately represented as Fe>> Zn> Cr, V> Ti> Mn> Co, Ni.

In most samples iron is found predominantly as Fe^{+2} in tetrahedral positions as detected by Mössbauer spectroscopy.

The spinel crystal system is cubic with the unit cell axis a_0 in the range 8.088-8.091A with a cell volume of 529.1-529.6$\mathring{A}^3$. The lattice constant increases with the size and concentration of substituted cations. The cell of natural $MgAl_2O_4$ decreases with increasing temperature.

Different types of transitions such as crystal field, exchange coupled and charge transfer transitions can be observed from the optical absorption spectra. transitions of Cr^{+3} at 17000-26000cm^{-1} in natural spinel are a strong evidence for the crystal field transitions. It has also been observed that spin forbidden electronic transitions of tetrahedral Fe^{+2} occur at 11000cm^{-1}.

The intensity of absorption bands in the range of 17000-26700cm^{-1} of the spinel decreases by approximately 30% on heating the sample from 293 to 1123K.