E2-31: Chemical and optical investigation on synthetic $MgAl_2O_4$ spinel doped with 3d transition metal ions

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The site preference for ions in spinel has been of considerable interest because the incorporation of these ions causes marked changes in properties such as colour, magnetism, cohesive energy and thermal conductivity. In this study electronic spectra and the oxidation state of doped elements in the spinel structure, were investigated.

Spinel crystals over 1 cm in size were grown both undoped and doped with the first period of transition elements at 1200°C by a flux grown method under controlled atmospheric conditions. $Na_2B_4O_7$ was used as a flux. The samples were allowed to cool to room temperature at a cooling rate of 1-2°C/h. The crystals thus formed were characterized using a Phillips PW1710 X-ray powder diffractometer. For chemical analysis a Cemeca SX50 automated electron microprobe was used. The valence states of the dopant ions were investigated using a Zeiss MPM 800 spectrophotometer equipped with halogen and xenon lamps.

Chemical analysis showed the presence of 65-70% wt Al_2O_3 and 25- 28% wt MgO. Concentrations of the transition metal oxides were in the range 0.8-10% wt.

Two broad intense bands occurred for the spin allowed transitions with high absorption coefficients in octahedrally co-ordinated Cr^{3+} ions. The spectrum of V bearing spinel consisted of 3 strong absorption bands in the visible region which were assigned to ligand field transitions of V^{3+} in octahedral or distorted octahedral oxygen polyhedra. The optical spectrum of Fe^{3+} doped spinel shows spin forbidden bands with very narrow and sharp absorption maximum. Three spin allowed absorption peaks were observed for Co^{2+} doped spinel in the tetrahedral co-ordination site. Very strong spin allowed bands with high extinction coefficients were observed for the Ni^{2+} bearing spinel. It was deduced that the high energy band of the Ni^{2+} was in the octahedral co-ordination. Absorption spectra of Mn^{2+} doped sample was dominated by 3 intense bands and these were assigned to spin allowed d-d transitions.

The variety of colours in spinel was due to the relative concentration of the doped elements. Most of the doped transition metal ions were accommodated in the 6-co-ordinated octahedral symmetry. The empirically established co-ordination for the 3d ions cannot be completely correlated with the preference energies calculated on a crystal field basis alone.

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