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Distribution of manganese ions in magnesium–aluminium spinels of different stoichiometries

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Abstract

Cathodoluminescence (CL), photoluminescence (PL) and EPR spectra of natural and synthetic spinels have been measured. CL spectra reveal two emission bands caused by transitions within Mn^{2+} ion. Relative intensities of green and red emission of Mn^{2+} have been compared during simultaneous excitation of tetra- and octa-coordinated manganese ions under electron beam. Growth of relative intensity of Mn^{2+} CL in tetrahedral sites has been found in common with decrease of manganese relative concentration. A peculiar Mn-associated PL, which is typical for $3d^3$ ions, has been observed in lilac natural spinel. Proceeding from position of optical band, the corresponding coordination has been chosen. Simulating EPR spectra have been used to estimate the degree and kind of disorder of nearest neighbours of Mn^{2+} ions.

1. Introduction

There is an enormous number of individual compounds and systems that can justifiably be classified as spinel. Ceramics based on the magnesium–aluminium spinels is candidate material for fission reactors in order to take advantage of their special properties [1]. Spinel single crystals are used for substrate in integrated electronics [2]. At various research institutions, magnesium–aluminium spinel doped with transition metal ions is under consideration as a laser material [3–5]. So, the material requires definite spectroscopic characteristics of impurity ions incorporated (e.g. Ref. [3]). Their optical absorption overlaps some bands of structure defects. Analysis carried out by means of luminescence and absorption spectroscopy should assist to distinguish the influence of impurity ions and other defects. These are the manganese ions, which have numerous channels of luminescence [6] and ESR spectra rich in components [7], and, thus, let to elucidate a short-range disposition in disordered materials very carefully.

Processing of synthetic magnesium–aluminium spinel allows easily to obtain both stoichiometric and nonstoichiometric spinels [8]. The latter may be described as spinel enriched with aluminium oxide while the composition does not denote a mixture of stoichiometric spinel and aluminium oxide grains. A gradual passage from surplus aluminium to normal stoichiometric spinel is interesting on the microscopical level, taking into account Al_2O_3 sintering techniques where the microstructure of oxide–substrate interfaces is of great importance [9].

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