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Long-lifetime fluorescence and crystal field calculation in Cr⁴⁺-doped Li₂MSiO₄, M = Mg, Zn

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Abstract

The diffuse reflectance spectra of Cr:Li₂MSiO₄, M = Mg, Zn, indicate that in these compounds, chromium ions occur in the 4+, 5+, and 6+ oxidation states simultaneously. Under selective excitation in a Cr⁴⁺ absorption band, a very long fluorescence decay time is observed for both compounds: ~110 μs at room temperature and ~300 μs at 30 K. These are by far the longest fluorescence lifetimes reported for Cr⁴⁺ activated materials. In Cr⁴⁺:Li₂MSiO₄, the ¹E excited state level lies below the lowest component of the ³T₂ level and the fluorescence decay time is dominated by the long-lifetime ¹E level for which the transition to the ground state is spin-forbidden. The reverse situation occurs for the other Cr⁴⁺ doped compounds and their fluorescence lifetimes, governed by the short-lifetime ³T₂ state, are only a few microseconds. A crystal field calculation, performed for Cr⁴⁺:Li₂MSiO₄, confirms the above interpretation and supports the localization of Cr⁴⁺ at the silicon site in this compound.

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1. Introduction

Tetravalent chromium activated crystals with tetrahedral symmetry, such as forsterite Cr⁴⁺:Mg₂SiO₄ [1,2] and Cr⁴⁺:YAG [3], are widely used as tunable solid state lasers in the near-infrared (1.2–1.5 μm), as saturable absorbers for passive Q-switching of neodymium lasers [4] and for ultra-short laser pulses generation [5]. Throughout this

paper, we will use the formal oxidation states for the chromium ions, although it is well known that their effective charges are much lower, due to the strong covalence of Cr–O bonds for chromium high oxidation states.

In YAG and forsterite, both tetrahedral and octahedral sites are available, and chromium may enter the lattices in the form of octahedral Cr³⁺, tetrahedral Cr⁴⁺ and sometimes as octahedral Cr⁴⁺. It follows that only a few percent of the chromium in these materials correspond to the tetrahedral Cr⁴⁺ active species [6,7].

In order to minimize this chromium tendency to occur with several oxidation states and to occupy

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