Luminescence of cerium doped $Mg_4Nb_2O_9$ phosphor

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The luminescence of complexes consisting of a highly charged transition metal ion having no outer d-electrons surrounded by a number of oxygen ions has been studied extensively due to their practical applications as phosphors. New interest in the luminescence of complexes of this kind was kindled when it was realized that rare-earth activated tungstates and vanadates were very good materials as laser host [1]. Among these complexes, niobium related complex such as NbO_6 has not been studied thoroughly to date. Nb^{5+} ions occupy octahedral sites in niobates and oxides. These niobate octahedra share faces and edges in various niobium containing compounds. Especially in the $Mg_4Nb_2O_9$ structure, two niobate octahedra share faces and $Mg_4Nb_2O_9$ shows very efficient luminescence [2]. The first luminescence of $Mg_4Nb_2O_9$ was reported by Wachtel [3]. The luminescence of $Mg_4Ta_{2-x}Nb_xO_9$ has been investigated by Macke [4]. In this letter we report the first luminescence study of cerium doped $Mg_4Nb_2O_9$ phosphor. Also, we report the substitutional site of cerium in $Mg_4Nb_2O_9$.

Samples were synthesized through the conventional solid state reaction technique. The starting materials were Nb_2O_5 and $MgCO_3$. The firing temperature was 1250 °C and firing time was 4 h. The phases of synthesized samples were checked through X-ray diffraction (XRD) against the existing Joint Committee on Powder Diffraction Standard (no. 36-1381). The luminescence spectra were obtained using a 75 cm Spex monochromator and the 254 nm Hg line was used as an exciting source.

The luminescence spectra of $Mg_4Nb_2O_9 \cdot Ce_x$ are shown in Fig. 1. The pure $Mg_4Nb_2O_9$ are due to two kinds of centres, namely a regular and a defect niobate octahedra [4]. The strong 420 nm emission band originates from the regular octahedra and the weaker emission band at 520 nm originates from defect octahedra. The $Mg_4Nb_2O_9$ has an ordered corundum structure where the pentavalent cations form pairs by face sharing of their coordination octahedra [5]. The defect niobate centre can be viewed as a partial disorder of the Mg^{2+} and Nb^{5+}
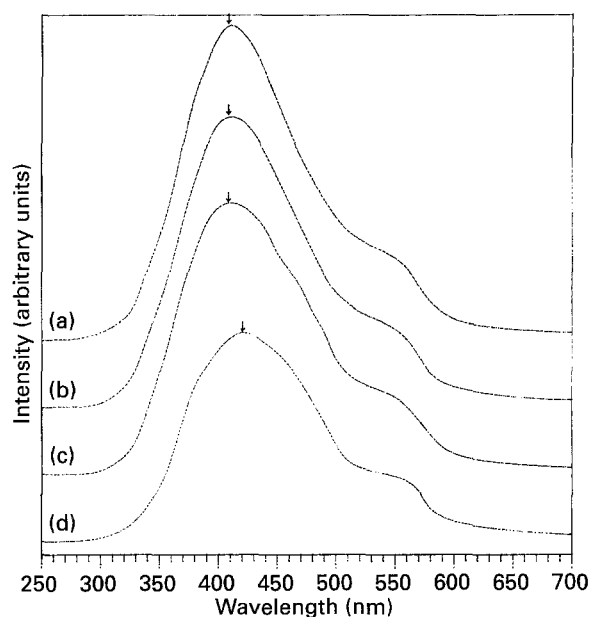
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Figure 1 Photoluminescence spectra of $Mg_4Nb_2O_9 \cdot Ce_x$. (a) $Mg_4Nb_2O_9 \cdot Ce_{0.003}$, (b) $Mg_4Nb_2O_9 \cdot Ce_{0.004}$, (c) $Mg_4Nb_2O_9 \cdot Ce_{0.005}$ and (d) pure $Mg_4Nd_2O_9 \cdot Ce$.

ions on the cation sites such that there exist Mg^{2+}–Nb^{5+} pairs instead of Nb^{5+}–Nb^{5+} pairs. When we doped 0.3 mol % of cerium in $Mg_4Nb_2O_9$, the intensity of the blue emission band (420 nm) was enhanced and the peak shifted to the short wavelength region. Also, the green emission band shape changed more significantly. Thus we can conjecture that the substitutional site of cerium in $Mg_4Nb_2O_9$ is the niobate site. The reasoning can be traced as follows. When the Nb ion is substituted with the Ce ion in $Mg_4Nb_2O_9$, the ionic size of the Ce ion is larger than that of the Nb ion such that it causes strain over the entire structure, which exhibits the blue shift in both emission bands. The enhancement of emission intensity of both emission bands gives more supporting evidence, since emission of the lowest crystal field components of 5d states of cerium lies between 385 nm and 415 nm in most oxide compounds [6]. Thus, the cerium substituted with niobium in $Mg_4Nb_2O_9$ causes resonant radiative energy transfer from cerium to niobium and it

enhances the niobium related emission in $Mg_4Nb_2O_9$. The third supporting evidence comes from the cerium concentration dependent emission intensities in our study. When we doped 0.4 mol% of cerium in $Mg_4Nb_2O_9$, the emission intensity decreased due to the self-absorption between Ce^{3+} pairs in this site. In other words, the self-absorption is blocking the energy transfer between Ce^{3+} to Nb^{5+} in this site. Further increase of the concentration of cerium in $Mg_4Nb_2O_9$ causes a more drastic decrease in emission intensity (see Fig. 1). The foregoing arguments support the substitution of cerium with niobium in $Mg_4Nb_2O_9$.

In summary, we report the first luminescence of cerium doped $Mg_4Nb_2O_9$ phosphor and our study indirectly reveals that the substitutional site of cerium in $Mg_4Nb_2O_9$ is the niobium site in this structure.

References

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