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Discussion

Response to "Comment on 'Distribution of oxidation states of Cr ions in Ca or Ca/Mg co-doped Cr:$Y_3Al_5O_{12}$ single-crystal fibers with nitrogen or oxygen annealing environments' by C.–N. Tsai et al." [J. Crystal Growth 310 (2008) 2774]

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It is well known that the fluorescence from chromium-ion-doped material depends significantly on its local matrix structure, composition, and the co-dopants because of its partially filled 3d electronic configuration that experience considerable interaction with the crystal field [1–3]. Cr^{4+} fluorescence intensity was found to decrease and shift to lower wavelength in the $Y_3Al_5O_{12}$ (YAG)-silica inter-diffusion layer [3]. Reducing and oxidation annealing can change the ratio of Cr^{4+}/Cr^{3+}, but the details of this process was not studied and understood well due to the complexity of processes with chromium participation in co-doped garnets. Our previous work [4] was the first attempt to unravel the details quantitatively.

The fluorescence intensities of Cr^{3+}_{oct} and Cr^{4+}_{trtr} (Cr^{3+}_{oct} is a triply ionized chromium occupying octahedral sites, Cr^{4+}_{trtr} is a quarterly ionized chromium occupying tetrahedral sites of the YAG matrix) depend not only on the concentrations of ion species but also on their emission cross sections. With better crystal quality by annealing, it is possible that both fluorescence intensities of Cr^{3+}_{oct} and Cr^{4+}_{trtr} increase due to enhanced emission cross-sections instead of increase in ion concentrations. The derived oxidation/reduction of Cr ions in YAG is based on the fact that quenching is not significant for the samples with or without annealing treatments. The radiative lifetimes of Cr^{4+} in samples being measured were in the range 3.1–3.5 μs, which is consistent with that of the bulk Cr^{4+}:YAG crystal.

To quantitatively estimate the concentrations of Cr^{3+}_{oct}, Cr^{4+}_{oct} and Cr^{4+}_{trtr}, some previous knowledge about the reaction formulas is needed [5,6] (i.e. Refs. [15,17] in Ref. [4]). In addition, it is observed that the reducing annealing in H_2 described in Ref. [7] (i.e. Ref. [16] in Ref. [4]) has similar behavior as annealing in nitrogen, though the detailed mechanism may not be the same.

The ionic radii of Cr^{6+}_{trtr}, ranging from 30 to 40 pm for various oxides and fluorides [8,9], were not specifically for YAG. It is much smaller than that of Cr^{4+}_{trtr}. We appreciate the comments of Feldman, Burshtein, and Shimony for pointing out this error, though we all agree that Cr^{6+}_{trtr} ions in YAG are rare especially when divalent co-doping level is not high as mentioned in Refs. [10,24] of Ref. [4].

References

[1] A. Sugimoto, Y. Nobe, K. Yamagishi, J. Crystal Growth 140 (1994) 349.
[2] S.A. Markgraf, M.F. Pangborn, R. Dieckmann, J. Crystal Growth (1997) 81.
[3] J.C. Chen, K.Y. Huang, C.N. Tsai, Y.S. Lin, C.C. Lai, G.Y. Liu, F.J. Kao, S.L. Huang, J. Appl. Phys. 99 (2006) 093113.
[4] C.N. Tsai, K.Y. Huang, H.J. Tsai, J.C. Chen, Y.S. Lin, S.L. Huang, Y.S. Lin, J. Crystal Growth 310 (2008) 2774.
[5] L.I. Krutova, N.A. Kulagin, V.A. Sandulenko, A.V. Sandulenko, Fiz. Tverd. Tela. (Leningrad) 31 (1989) 170;
L.I. Krutova, N.A. Kulagin, V.A. Sandulenko, A.V. Sandulenko, Sov. Phys. Solid State 31 (1989) 1193.
[6] A.G. Okhrimchuk, A.V. Shestakov, Opt. Mater. 3 (1994) 1.
[7] S.B. Ubizskii, S.S. Melnyk, B.V. Padlyak, A.O. Matkovskii, A. Jankowska-Frydel, Z. Frukacz, Proc. SPIE 4412 (2001) 63.
[8] R.D. Shannon, C.T. Prewitt, Acta. Crystallogr. B 25 (1969) 925.
[9] 〈http://www.webelements.com/chromium/atom_sizes.html〉.

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