

OPTICAL PROPERTIES OF Tm DOPED LiNbO₃ AND LiNbO₃ (MgO)

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Abstract- The optical properties of Tm doped LiNbO₃ and LiNbO₃:MgO, especially within the $^3H_6 \rightarrow ^3H_4$ transition, have been studied. Differences in the absorption spectrum and particularly in the emission spectrum of Tm in both crystals are observed. New bands with different polarization character appear in the MgO doped crystals, indicating the existence of Mg-perturbed Tm sites.

1. - Introduction

Rare earth doped crystals have received an early attention (1) as laser crystals because of the potentialities of combining in a single medium the laser emission with the electro-optic and non-linear properties of the matrix.

The possibility of reducing the photorefractive damage by the addition of MgO (2) and the efficient laser operation in waveguide structures (3-4) has considerably widened the interest of these crystals. Nevertheless, the interaction between the active rare earth ions with the stabilizing Mg has begun to be considered only very recently (5).

In this work the effect of MgO codoping on the optical properties of Tm doped LiNbO₃ has been studied, with particular attention to the $^3H_4 \rightarrow ^3H_6$ transition (1.8 μ m), due to its interest as potential broadly tunable laser operation (6).

2. - Experimental procedure

LiNbO₃:Tm and LiNbO₃:Mg,Tm crystals were grown along the C-axis by the Czochralsky method from grade I Johnson-Mathey powder. Tm concentration (relative to Nb) in the crystals was 1.0 % and 0.4 % molar fraction respectively, and MgO was added in a ratio of 6.0 % molar fraction.

Absorption spectra were taken with a Cary 14 spectrophotometer. An Ar-pumped Ti:Sapphire laser (Spectra Physics 3900) was used to excite the luminescence which was detected with a Peltier cooled germanium detector (Judson J16) after being dispersed by a 30 cm focal length monochromator (Mc Pherson 218).

3.- Results and discussion

The absorption spectrum of Tm^{3+} ions in $\text{LiNbO}_3:\text{MgO}$ is basically coincident with that obtained in LiNbO_3 (no MgO) (1) and has been omitted for the sake of brevity.

The most relevant change is a strong reduction in the absorption coefficient ($\times 0.4$) in the MgO codoped crystals for equal Tm concentration in the melt. This inhibiting effect in the dopant incorporation is opposite to that one found for other rare earths (7) and it is a first signal of the interaction between Mg and Tm ions.

Changes in the absorption spectrum due to MgO codoping can be detected after a closer inspection at low temperatures, as can be seen in figure 1, where the absorption bands associated to the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ transition for Tm and Mg,Tm doped samples at liquid helium temperature (LHT) are shown. The room temperature spectra have been also included to illustrate the thermal broadening of the spectra.

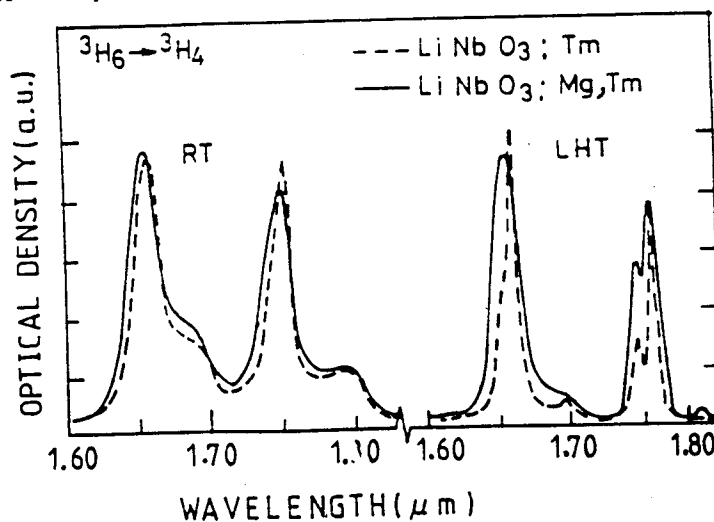


Figure 1: Comparison of the normalized $^3\text{H}_6 \rightarrow ^3\text{H}_4$ absorption bands for Tm (---) and Mg,Tm (—) doped LiNbO_3 .

It can be seen that Tm doped crystals exhibit a narrower spectrum, where several peaks at 1.652, 1.660, 1.696, 1.745 and 1.756 μm ($E_1 = 6052, 6025$,

5897, 5731 and 5695 cm^{-1}) can be distinguished.

Rare earth ions are reported to incorporate into LiNbO_3 at Li^+ and Nb^{5+} sites (8), both having C_3 symmetry. In this symmetry a $^3\text{H}_4$ multiplet splits into 6 sublevels (9), which could, in principle, account for the observed structure.

Comparing Tm and Mg,Tm doped crystals it can be seen that the same structure remains in the Mg,Tm doped crystal, although somehow blurred because of the apparent line broadening. It is also apparent that the relative heights of the different sub-bands within the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ transition have changed.

This fact would be hardly explained by the assignment of the observed structure to single-site sublevels and it suggests, in analogy with other rare earths (5,10), that these effects could be attributed to the appearance of Tm ions in various sites (Li or Nb) being its relative occupancy affected by the incorporation of Mg, which is located preferentially into Li sites (5).

Nevertheless, the most dramatic changes between Tm and Mg,Tm doped crystals are detected in the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ emission spectrum. This luminescence can be observed after excitation into the $^1\text{G}_4$ or $^3\text{F}_4$ multiplets, which partially decay to the $^3\text{H}_4$ level. The $^3\text{H}_6 \rightarrow ^1\text{G}_4$ and $^3\text{H}_5 \rightarrow ^3\text{F}_4$ absorption bands conveniently overlap with the Ar^+ and Ti:Sapphire laser emissions respectively, which can be used to excite efficiently the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ luminescence.

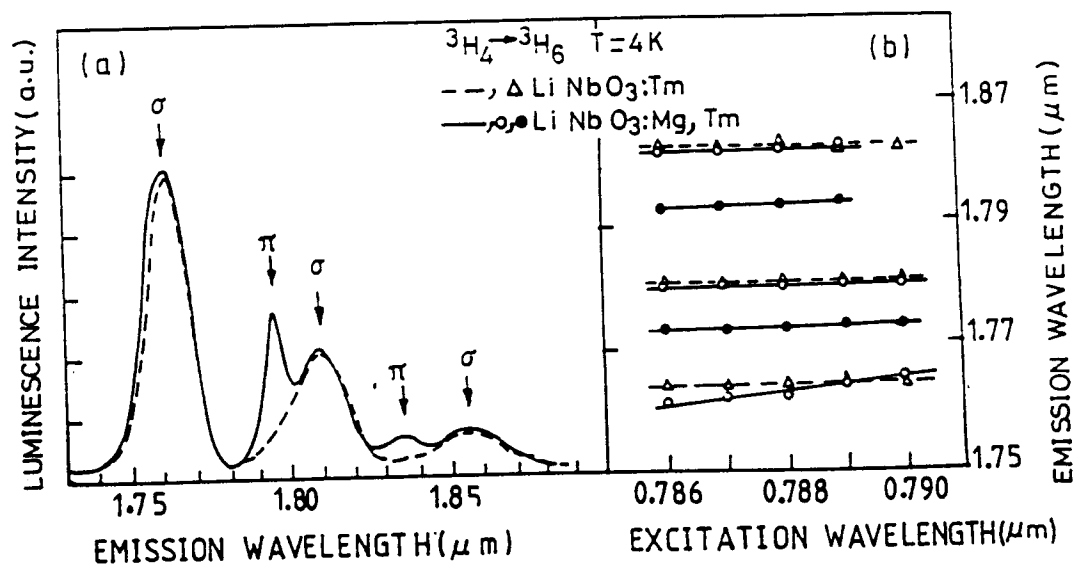


Figure 2: (a) Emission spectra associated to the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition in the wavelength range $1.73 \mu\text{m} < \lambda < 1.88 \mu\text{m}$.
(b) Peak position of the different bands within the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition for Tm (o, Δ) and Mg-Tm (\bullet) sites.

Figure 2a shows the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ emission spectrum at 4 K for Tm and Mg,Tm doped LiNbO_3 , in the range $1.73 \mu\text{m} < \lambda < 1.88 \mu\text{m}$, after excitation into the ${}^3\text{F}_4$ multiplet, at around 800 nm, by using the Ti:Sapphire laser. The same spectrum is obtained after Ar-laser excitation into the upper ${}^1\text{G}_4$ level.

It can be seen that Tm doped crystals exhibit three emission bands at 1.764, 1.810 and 1.855 μm plus a shoulder at 1.758 μm , indicating Stark levels in the ${}^3\text{H}_6$ ground state at 20, 165 and 296 cm^{-1} , in accordance with the values reported by Johnson and Ballman (1). The same bands are also present in Mg,Tm doped crystals, but in addition two new bands at 1.795 μm and 1.836 μm appear, indicating the incorporation of Tm ions into sites strongly influenced by Mg ions, as already observed in Mg,Nd doped crystals (5), and that we shall denote consequently as Tm-Mg sites.

The peak positions of the emission bands do not change appreciably within the excitation band (figure 2b) except for a small change in the emission at 1.764 μm , revealing some minor structure; and the excitation spectra of Tm and Tm-Mg sites are only slightly displaced, peaking at around 787 nm.

Another interesting feature is the polarization character of the emission bands. Whereas the Tm-related bands exhibit a σ polarization, the new Tm-Mg sites exhibit a clear π polarization. This change in polarization character, seems to indicate that the new centers have a markedly different orientation.

Finally the lifetime (broadband) of the ${}^3\text{H}_4$ level has also been measured in the temperature range 4-300 K. A temperature independent value of 3 ms has been obtained for both Tm and Mg,Tm doped crystals. This long lifetime indicates that non-radiative relaxation to the ground state are unimportant, suggesting a high luminescent quantum efficiency for the transition.

4. - References

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