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Luminescence properties of $KNbO_3$ crystals

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Abstract

Thermostimulated luminescence, X-ray-induced luminescence, photostimulated luminescence as well as the time-resolved luminescence and absorption after pulsed electron beam irradiation were studied in $KNbO_3$ crystals at 80–400 K. A correlation between defects causing the luminescence and blue-light-induced IR absorption effects supressing the second harmonic generation efficiency in $KNbO_3$ is discussed.

Keywords: Time-resolved spectroscopy; Radiation-induced defects; $KNbO_3$

1. Introduction

$KNbO_3$ crystals are widely used in optical applications, for example, for second harmonic generation. However, the efficiency of this process is strongly affected by the presence of impurities and crystal defects. In particular, the effect of blue-light-induced IR absorption (BLIIRA) was observed [1]; the nature of defects responsible for this effect is not clear. In this paper, the luminescence of $KNbO_3$ crystals is studied in order to understand the nature of radiation-induced defects and impurities and how do they affect the optical properties.

Until now, the luminescence of alkali niobate oxides was mainly studied for $LiNbO_3$ [2–4]. The main intrinsic luminescence centers are the regular niobate groups (the band peaking at 2.9 eV with $\tau = 130$ μs at 5 K) and the distorted niobate groups (2.38 eV with $\tau < 80$ ns at 5 K). $KNbO_3$ is much less investigated, but the niobate group luminescence is observed here too [5]. Despite the fact that the defects in oxygen sublattice were observed in reduced $KNbO_3$ crystals and Fe-doped crystals (F-type centers) [6], their luminescence is not yet studied.

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2. Samples and experimental methods

$KNbO_3$ crystals (pure and 0.1% MgO-doped) obtained from Virgo Optics Inc., Florida, were studied and results of the BLIIRA investigation for these samples were reported [1].

Different excitation sources were used: X-rays (40 kV, 10 mA), N_2-laser (3.67 eV, 10 ns pulses) and pulsed electron beam (0.27 MeV, 10 ns). The time-resolved experiments were described in Ref. [7].

3. Results and discussion

Three luminescence bands (2.03, 2.53 and 2.85 eV) are observed in all the studied samples.

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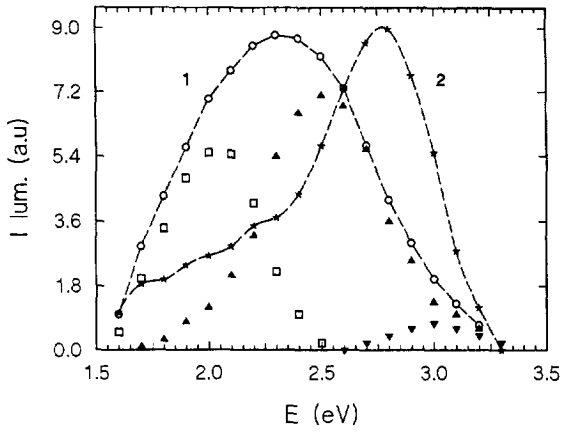

Fig. 1. Luminescence spectra of $KNbO_3$ observed under X-ray irradiation (1) and pulsed electron beam irradiation (2) at 300 K. Three Gaussian elementary components peaking at 2.03 eV (□), 2.53 eV (△) and 2.85 eV (▽) are shown. Spectrum (2) is measured 30 ns after the irradiation is switched off.

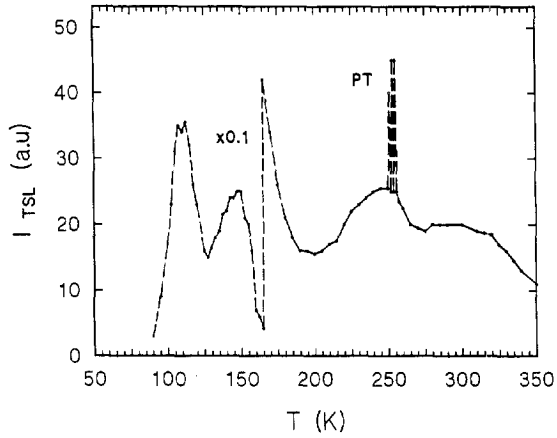

Fig. 2. TSL after X-ray irradiation at 80 K during 1 h (heating rate is 0.2 K/s).

Their particular contributions to the total spectra depend on the excitation type, impurity content and temperature. The typical spectra observed under X-ray and electron beam irradiation for pure $KNbO_3$ crystal are shown in Fig. 1. The 2.03 eV luminescence band dominates in powders and destroyed samples and could be due to the surface and grain boundary defects. In turn, the 2.53 and 2.85 eV luminescence peaks are caused likely by the intrinsic luminescence from Nb-groups. Three exponential components with lifetimes 30, 70 and 180 ns could be distinguished in the 2.3 eV photoluminescence decay kinetics measured at 80 K for all samples. According to Ref. [5], the band with lifetime of $\tau \sim 500$ ns (at 60 K) corresponds to $(NbO_6)^{7-}$ group, which is close to our result (180 ns at 80 K). The transient absorption band extended from 1.2 to 2.3 eV was observed after pulsed electron beam irradiation. The luminescence spectra 2 shown in Fig. 1, were measured 30 ns after pulsed electron irradiation and could be affected by the reabsorption effect.

The thermostimulated luminescence (TSL) was measured after X-ray irradiation at 80 K; typical TSL curve is shown in Fig. 2. Rich shallow trap spectra at 100–120 and 130–160 K are observed and could be associated with uncontrolled impurities. The TSL at 200–260 K consists of a broad peak with a series of very sharp peaks at 252–256 K. The latter arise due to phase transition (PT) – a change of lattice configuration around the defects leads to electron/hole delocalization from traps. The TSL peak at 350 K demonstrates that *stable* defects could be created under X-ray irradiation at room temperature. Taking into account that in this temperature region the partial annealing of F-type centers occurs [8], we suggest that this high-temperature peak results from the recombination of released holes with F-type centers. For the samples, preliminary irradiated with an electron beam, two broad absorption peaks at ~ 1.7 and ~ 2.7 eV were observed. The nature of these centers is still an open question. The simplest mechanism of the observed BLIIRA effect could be the UV absorption in F- and F^+- center bands which lead to their ionization and thus electron/hole transfer to the defects revealing IR absorption.

Acknowledgments

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