



Low temperature X-ray luminescence of KNbO₃ crystals

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Abstract

We have studied X-ray luminescence of KNbO₃ single crystal. The 575 nm luminescence band has been studied in the temperature range of 15–45 K. The quenching parameters were found to be $Q = 12 \pm 3$ meV and $\nu = 4 \times 10^{11}$ s⁻¹. No luminescence has been observed under heavy ion excitation (⁸⁶Kr ions, 8.63 MeV/amu) even at 15 K. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The niobate single crystals MNbO₃ (M = Li, Na, K) are of a great interest for modern technology because of their good electro-optic, non-linear optic and acousto-optic properties. Among them potassium niobate (KNbO₃) is a primary candidate for many applications in the fields of optical signal processing, dynamic holography, and optical frequency conversion [1,2].

The luminescence properties have been described in detail only for doped and undoped LiNbO₃ [3–11]. The luminescence properties of LiNbO₃ depend strongly on the stoichiometry of samples. Two emission bands have previously been reported in lithium niobate. Stoichiometric sam-

ples and crystals doped with magnesium show the emission band with a maximum at about 440–450 nm, which has been ascribed to recombination luminescence of an O⁻ hole with Nb⁴⁺ electron [3–10]. The Li-deficient samples show an emission band with a maximum at about 520 nm which has been attributed to a similar luminescence process in which the Nb⁴⁺ occupies a lithium site [5,11].

Luminescence of potassium niobate crystals has been previously reported in [10,12–16]. Two photoluminescence bands at 420 and 530 nm have been reported in powders of KNbO₃ [10], where these two bands have been ascribed to self-trapped exciton emission from the NbO₆ octahedron of two different crystal modifications of KNbO₃ [10,14]. It was indicated that the quenching temperature (at which the luminescence intensity has decreased by 50% of the intensity at liquid helium temperature) for 420 and 530 nm emission bands were 70 and 35 K, respectively. Photo- and X-ray

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luminescence of single crystals KNbO_3 in the 35–160 K temperature range has been reported in [12]. The photoluminescence at 550 nm was observed only at temperatures below 45 K, whereas X-ray induced luminescence consisted of two overlapping bands peaking at 505 and 540 nm. Two later emission bands were completely quenched above 160 K. Three luminescence bands at 550, 495 and 410 nm have also been observed below 100 K in [15].

In this paper we have studied X-ray luminescence of KNbO_3 single crystal. The aim of our study was extending the temperature range down to 10 K and to measure the temperature dependence of a long-wavelength luminescence band in order to determine its quenching parameters. We have also studied the effects of heavy ion irradiation on the optical properties of KNbO_3 crystals.

2. Experimental

Pure KNbO_3 crystal grown by Virgo Optics Inc., Florida has been studied. The apparatus used for this work is essentially the same as that previously described in [17,18]; we shall therefore give only a very brief description here. X-ray or ion-induced luminescence is analysed, in the 200–800 nm range with Jobin–Yvon monochromator and detected in the photon counting mode. The chromatic response of the monochromator and photon detector is measured using a calibrated tungsten lamp and deuterium lamp. The shape of the spectra is corrected for the measured transmission function. The optical absorption measurements were performed with a double-beam Perkin Elmer spectrophotometer in the wavelength 200–900 nm range with a 4 nm resolution. Crystals have been irradiated at GANIL on the medium energy beam line (SME) with ^{86}Kr ions (8.63 MeV/amu).

3. Results and discussion

During X-ray irradiation of KNbO_3 crystals, a broad luminescence band with the peak at 575 nm is observed (Fig. 1). The temperature dependence of X-ray luminescence was investigated, monitor-

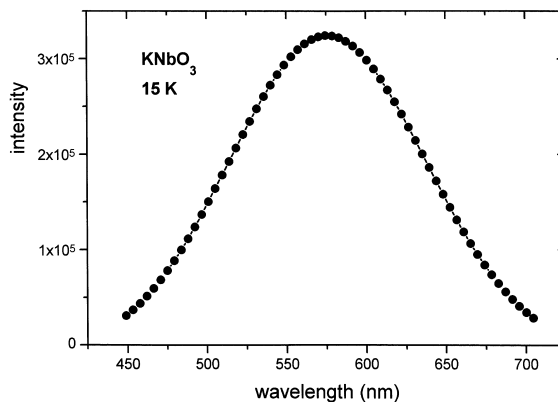


Fig. 1. Luminescence spectrum of KNbO_3 under X-irradiation at 15 K.

ing spectra between 15 and 45 K (Fig. 2). We have found that the 575 nm emission is quenched above 30 K. Analysing the luminescence yield between 10 and 45 K, we have determined the quenching parameters Q and ν . The thermal activation energy Q is calculated from the energetic yield η using the Mott and Seitz formula,

$$\eta = \left(1 - \nu\tau \exp(-Q/kT)\right)^{-1}. \quad (1)$$

Plotting of $\log[(1/\eta) - 1]$ as a function of $1/T$ gives a straight line. Its slope gives $Q = 12 \pm 3$ meV. Then, taking into account that $\tau \approx 100 \mu\text{s}$ [13] we find $\nu = 4 \times 10^{11} \text{ s}^{-1}$.

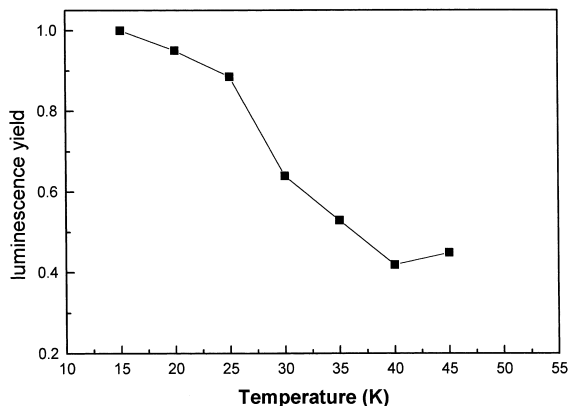


Fig. 2. Temperature dependence of the luminescence yield as a function of temperature.

By analogy with LiNbO_3 , we ascribe long-wavelength luminescence in KNbO_3 to the exciton recombination luminescence of an O^- hole with Nb^{4+} electron, where the Nb^{4+} occupies probably a potassium site. Then the luminescence quenching activation energy could be associated with the binding energy of the such exciton.

No luminescence bands have been excited at temperatures above 45 K, in agreement with [10,12], but in contradiction with [13,15,16]. A probable explanation of the above fact is that the Fe ion concentration in our sample is considerably lower than that in the samples studied in [13,15,16]. We have not observed luminescence in our KNbO_3 crystal in the course of heavy ion excitation (^{86}Kr ions, 8.63 MeV/amu) even at 15 K.

Irradiations of KNbO_3 with heavy ions were also performed at RT. No absorption bands were observed in the wavelength range from the absorption edge (326 nm, corresponding to the band gap of 3.8 eV) up to the near IR. Only fluence-dependent red-shift of the absorption edge and the appropriate increase of the absorption pedestal were seen. These are related to the simple light-diffusion effect resulting from the structural modifications induced by heavy-ion bombardment. A similar picture has been observed in LiNbO_3 [19] and TeO_2 [20]. However, in the case of fast electron irradiation with energies above 300 KeV in both materials Hodgson et al. [21,22] have observed a broad band in visible spectrum range probably due to F-type centre (oxygen vacancy). It is interesting to notice that for instance in MgO and Al_2O_3 F-type centres can be created not only under the electron irradiation [23,24], but also under irradiation with different ions [25–27]. One question is raised: why we did not see F centre production in LiNbO_3 , KNbO_3 or TeO_2 under ion irradiation, although they can be created in other oxides like MgO , Al_2O_3 . We believe that a very possible reason is ionization-induced annealing of vacancy-interstitial Frenkel pairs. We have to notice that although in oxide materials F centres are created via elastic collisions, the role of electronic excitations is very important. In particular, the ionization may lead to radiation-enhanced diffusion/annealing of the atoms/vacancies produced by nuclear collisions. Furthermore such effects should

be much more pronounced in materials where vacancy and (or) interstitial defects have low activation energies for diffusion. For instance, even in MgO , where intrinsic diffusion of both F centres, oxygen vacancies begins above 1000 C, with the corresponding migration energies of 2.5–3.3 eV [28], and oxygen interstitials start to anneal out at 350 C (the corresponding migration energy of 1.6 eV) [29], 50% F centre ionization-induced annealing under sub-threshold electron irradiation was observed [27]. In KNbO_3 the effects of ionization-induced and thermally assisted annealing of close Frenkel defects should be much more effective, due to very low oxygen vacancy migration energy of 0.7 eV [30], with appropriate migration temperature very close to RT. Probably the same reason is valid for TeO_2 , where oxygen vacancy migration energy is also as low as 0.42–0.54 eV [20].

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