

Obtaining and investigation of the LiNbO₃, LiNbO₃:Mg, LiTaO₃ nanopowders doped with Pr ions

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Summary:

The samples of LiNbO₃:Pr, LiNbO₃:Mg,Pr, LiTaO₃:Pr nanopowders were obtained by the high-energy ball milling with subsequent annealing. Pellets were prepared from nanopowders by pressing for further investigation. The photoluminescence properties were studied using the SOLAR CM 2203 spectrofluorometer. The luminescence spectra of obtained samples in the red region of the spectrum in shape and spectral position coincide with the data for LN:Pr and LT:Pr single crystals and micropowders.

Keywords: lithium niobate, lithium tantalate, Pr ions, nanopowders, photoluminescence

Introduction

Lithium niobate (LiNbO₃, LN) and lithium tantalate (LiTaO₃, LT) single crystals doped by Pr ions have been attracting the attention of researchers since the 1990s [1, 2]. The reason for this is great interest in using of extraordinary physicochemical properties of LN and LT crystals in order to create multifunctional active elements for optoelectronic devices and sensors. In this context the results of recent years concerning the phenomenon of piezoluminescence in LN:Pr and LT:Pr are of particular interest to create, for example, a pressure sensors [3, 4]. It was found that the most intense mechano- and photoluminescence is observed in stoichiometric LN:Pr and LT:Pr samples. Also, attention was paid to the study of LN crystals, simultaneously doped by Pr and Mg [5]. Note that the investigation of the optical properties and photoluminescence of LN:Pr and LT:Pr was usually performed on single crystals of congruent composition grown by the Czochralski method. Whereas, the study of the mechano-luminescent properties of LN:Pr and LT:Pr was performed on samples of micropowders obtained by solid-phase synthesis from a mixture of the corresponding starting oxides and lithium carbonate. The

current work focuses on obtaining of LiNbO₃, LiNbO₃:Mg, LiTaO₃ nanopowders doped with Pr³⁺ ions by high energy ball milling and subsequent studies of luminescent properties of ceramic samples made from these powders.

Experimental details

Based on the results of [6] nanopowders with nominal compositions Li_{0.98}Pr_{0.02}NbO₃ (denoted as LN:Pr), Li_{0.93}Mg_{0.05}Pr_{0.02}NbO₃ (LN:Mg,Pr), Li_{0.98}Pr_{0.02}TaO₃ (LT:Pr) were obtained by high-energy ball milling of the corresponding powders mixtures (Li₂CO₃, Nb₂O₅, Ta₂O₅, MgO, Pr₆O₁₁) taken in molar ratios corresponding to stoichiometric compositions. The milling was carried out by using of the planetary ball mill of Pulverisette-7 type (Fritsch, Germany). The rotation speed was equal to 600 rpm, and the duration of milling was about 15 h. The precursors obtained after milling were annealed in air at 700°C for 5 h. The control of structural parameters of nanopowders was performed by the XRD method on a DRON-3 diffractometer with the subsequent refinement of the x-ray patterns by the Rietveld method. Pellets with 6 mm diameter and 1.2 mm thickness were prepared from nanopowders by pressing. The pressure was about 190 MPa. It should be

noted that two types of samples were made: three pellets with different composition (see above) were pressed under an applied electric field (voltage of 1 kV) with simultaneous heating to about 200 °C; another three samples were pressed without the applied electric field at room temperature. Subsequently all the obtained pellets were annealed in air at 600°C for 6 h. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were studied using the SOLAR CM 2203 spectrofluorometer.

Results

XRD analysis of nanopowders showed that they all contain only one phase, which corresponds to the LiNbO₃ structure. According to XRD data the particle size was estimated to be about 20...80 nm. Similarly to [3, 4] the luminescent studies were performed in the red region of the spectrum. The excitation wavelength was 270 (LN) and 250 (LT) nm. All samples exhibited the emission band with a maximum of about 620 nm (Fig. 1) attributed to the ¹D₂ → ³H₄ transition of Pr³⁺ [1].

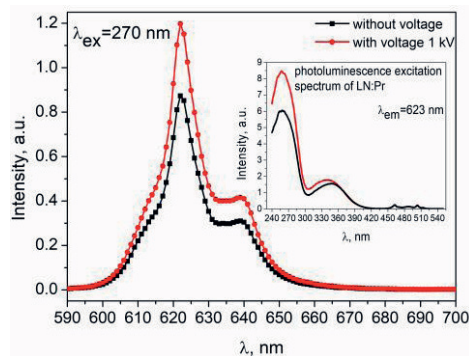


Fig. 1. The PL and PLE spectra of LiNbO₃:Pr

The most intense PL is observed in the LN:Pr samples (Fig. 1). Monitoring the 623 nm emission demonstrated that the excitation spectra were dominated by two broad UV bands centered at 258 and 345 nm (inset in Fig.1). Similar spectra of PL and its excitation were observed for both studied LN:Mg,Pr samples. The relative intensity of the PL was almost 10 times lower than that of the LN:Pr. There is a certain difference in the position of the UV excitation bands of red luminescence, namely, their maxima are shifted towards longer wavelengths compared to LN:Pr. In contrast to LN:Pr, in LT:Pr samples "red" luminescence has lower intensity, and its excitation bands at 240 nm and 290 nm are shifted towards shorter wavelengths (Fig. 2). Note that red luminescence in all samples is also excited in the processes of f-f transitions in Pr³⁺ ions, but the efficiency of such excitation is much lower than in the f-d transitions.

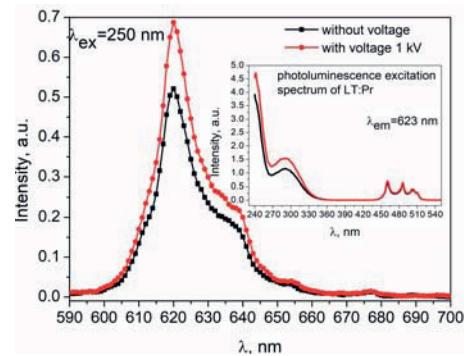


Fig. 2. The PL and PLE of LiTaO₃:Pr

Also, an important result is that the luminescence of Pr³⁺ and its excitation in the UV region are more intense in the samples, which were pressed under applied field and temperature.

Conclusions

The single-phase nanopowders with nominal compositions Li_{0.98}Pr_{0.02}NbO₃, Li_{0.98}Pr_{0.02}TaO₃ and Li_{0.93}Mg_{0.05}Pr_{0.02}NbO₃ were obtained by the high-energy ball milling with subsequent annealing. The method of sample preparation significantly affects the results. The samples pressed under the voltage demonstrate higher relative photoluminescence intensity. One of the reasons for this may be the higher ordering of nanoparticles of ferroelectrics in the electric field.

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