

Stable Color Centers Induced in Pure and Neodymium Doped $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$ Crystals by Gamma Irradiation

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The work is devoted to investigation of stable coloration induced by gamma radiation from ^{60}Co (1.25 MeV) in pure and neodymium doped $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$ single crystals. Nature of the induced absorption is discussed. This absorption is due to charge change of native defects or ions forming of crystals (vacancy, niobium ions, etc.). The nature of color centers responsible for induced absorption is discussed.

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1. Introduction

Ferroelectric crystals with the tetragonal tungsten bronze structure (TBS) are widely studied objects in physics of heterogeneous media. These systems are featured in a number of useful properties including piezoelectric, electro-optic, photorefractive, and pyroelectric ones [1, 2].

One of such materials is calcium barium niobate $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (CBN), which is better suited to potential applications, because it has a much higher phase transition temperature than popular strontium barium niobate (SBN) [3].

The effect of gamma radiation on TBS crystals was studied for SBN and changes of dielectric properties of this crystal was associated with the stabilization of the ferroelectric phase of the material in an internal bias field generated by radiation-induced defects [4]. In this way the study of radiation defects in TBS crystals is important. One of the approaches of such study is investigation of the absorption changes induced by ionizing irradiation. Up to now, the induced absorption changes were studied only in SBN:Ce and SBN:Cr under visible light irradiation [5, 6].

Therefore purpose of the present work was to study an effect of gamma irradiation on the optical absorption of TBS crystals, in particular pure and neodymium doped CBN single crystals.

2. Experimental

The pure and neodymium doped $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$ crystals were grown in the Institute of Electronic Materials Technology by the Czochralski technique. The concentration of neodymium ions was 1 at.%. Samples for

investigations were made in the form of plane-parallel polished plates of 0.9 mm thickness. The samples were irradiated with gamma quanta (1.25 MeV) from ^{60}Co and stored at room temperature in darkness. Optical absorption spectra were recorded with a Cary 5000 spectrophotometer. The value of additional absorption induced by the irradiation was determined as difference between the spectra after and before the irradiation.

3. Results and discussions

The optical absorption spectra of the as-grown CBN crystals are shown in Fig. 1. The fundamental absorption edge of the studied CBN crystals is observed above 27000 cm^{-1} that is close to the band gap of 3.65 eV reported for $\text{Ca}_{0.25}\text{Ba}_{0.75}\text{Nb}_2\text{O}_6$ films [7]. The absorption spectra of the CBN samples exhibit a small absorption coefficient values in the wave number range below 26000 cm^{-1} . This is an evidence of good optical quality of the studied crystals. However, the pure as-grown crystal demonstrates some small coloration (up to 1 cm^{-1}) in visible above 14000 cm^{-1} . On the other hand, the Nd-doped crystal looks like a perfect from the point of view of its transparency in visible region — only the sharp absorption lines caused by Nd^{3+} doping are observed here.

After irradiation of the crystals with gamma quanta at room temperature, a broad and complex additional absorption is observed in the UV-vis-nearIR region from 10000 to 27000 cm^{-1} (see Fig. 2). The value of the additional absorption that is observed after the used irradiation is relatively low (up to 0.6 cm^{-1}), however the structure of this additional absorption differ essentially for the pure and Nd-doped CBN crystals. The additional absorption spectrum of the pure crystal consists mainly of the complex bands around 17000 , 14000 and 12000 cm^{-1} as well as a weaker band at 25000 cm^{-1} . For the Nd-doped crystal, besides the similar bands around 17000 and 12000 cm^{-1} , the broad band at 21000 cm^{-1} is observed as a major one.

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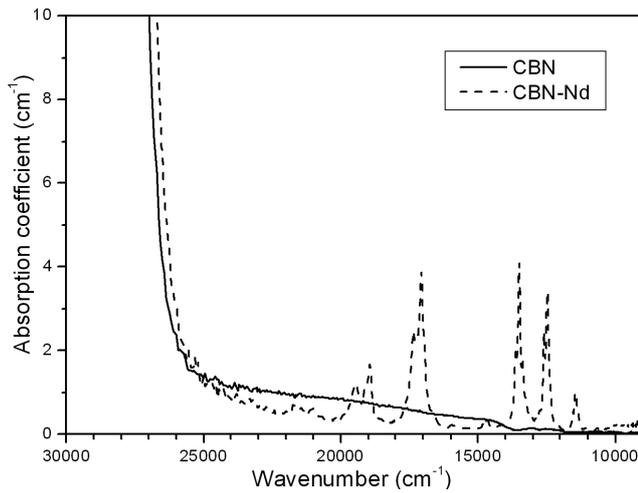


Fig. 1. Room temperature optical absorption spectra of the as-grown pure CBN and CBN:Nd crystals.

The observed additional absorption vanishes completely already after 15 min warming of the crystals in air at 373 K that proves their relatively low thermal stability.

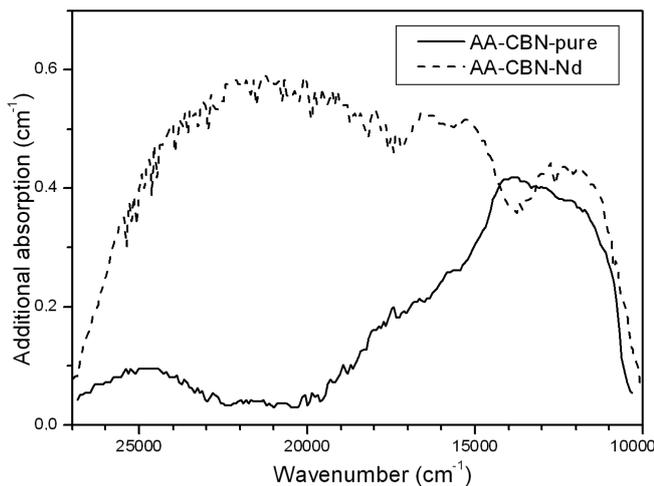


Fig. 2. Additional absorption spectra of pure CBN and CBN:Nd crystals after room temperature γ -irradiation up to the dose of 3×10^4 Gy.

The stable at room temperature absorption of complex oxide crystals in visible region is usually attributed to F-type color centers formed on the basis of oxygen vacancies [8–11]. Excitation of the material in this spectral range causes photoionization of these F-centers [8] and produces free electrons, which can be trapped by other electronic-type centers. In the case of the niobium containing crystals, the electronic polarons are associated with the Nb^{4+} centers. In accordance with Refs. [6, 12, 13], the Nb^{4+} polarons absorption in TBS and related crystals is observed around 6000–7000 cm^{-1} and is stable only at low temperatures. In such a way

it should not be observed in our experiment. The near-IR induced absorption of complex oxides can be also attributed to hole polarons (O^- centers), which are usually unstable in room temperature [13–15].

In work [16] it was shown that the basic crystal structure of CBN crystals at neodymium doping is not affected in comparison with pure CBN, but the number of oxygen vacancies increases. In such a way the induced absorption around 21000 cm^{-1} observed by us after γ -irradiation can be caused by F-centers created on the basis of the available oxygen vacancies.

An interpretation of the stable absorption induced in bands around 17000, 14000 and 12000 cm^{-1} is not clear. This absorption is very similar to the absorption induced in SBN:Ce crystals under visible light illumination [12]. In spite of the fact that this absorption has higher temperature stability in comparison with the absorption around 7000 cm^{-1} , its value goes to zero at room temperature [12]. The obtained absorption bands are relatively wide and most likely they could be represented as superposition of several overlapping bands belonging for different centers. By analogy with other complex oxides, the induced absorption around 16000 cm^{-1} that is stable at lower temperatures can be related to bound hole polarons absorption [14, 15]. Possibly a residual value of much higher absorption of hole polarons is observed by us at room temperature. We note that for example in garnets the presence of stable O^- polarons near defects in cation sublattice (defects bound polarons) is possible in room temperature [9], but their absorption lies in high energy area of the spectrum. It was shown for bound hole polarons that their absorption is shifted to higher wave number in comparison with free electron polaron and the position of absorption band of bound hole polaron strongly depends on kind of point defects [13]. Additionally, polaron aggregates (for instance bi-polarons) could be created under irradiation. Stable and transient absorption of electron bipolarons were observed for example in LiNbO_3 crystals with maximum of absorption in visible area [17–19]. Presence of $\text{Nb}^{4+}\text{-Nb}^{4+}$ bipolarons would explain no evidence of electron polaron band in our experiment.

To clarify this situation, additional studies of thermal and time stability of the absorption induced by high energy irradiation are required.

4. Conclusions

The gamma irradiation of CBN crystals produces an additional absorption in UV-vis-nearIR region from 10000 to 27000 cm^{-1} that is metastable at room temperature. The thermal stability of this coloration is relatively low — it vanishes completely already after 15 min warming of the crystals at 373 K. The additional absorption differs in case of undoped and Nd doped material. This difference may be due to appearing of more F-type centers in Nd doped CBN, because neodymium doping increases number of oxygen vacancies.

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