Time Decay of Stable Absorption of Gamma Irradiated LNO, LNO:Cu and YAP:Ce Crystals

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(Received December 6, 2013; in final form March 26, 2014)

The present work is devoted to investigation of stability of stable color centers that are induced by gamma radiation in pure $LiNbO_3$, Cu-doped $LiNbO_3$ and Ce-doped $YAlO_3$ single crystals

DOI: 10.12693/APhysPolA.126.774
PACS: 61.80.–x, 78.40.–q, 61.72.jn

1. Introduction

Lithium niobate $LiNbO_3$ (LNO) is a ferroelectric crystal having important applications in laser, electrooptic, acoustooptic and optical storage devices [1, 2]. The photo-refractive effect, which is used for storage of volume phase holograms, is due to the presence of transition metal impurities (for example Cu) and intrinsic lattice defects [2, 3], which are sources and traps of electrons in lithium niobate crystals. Yttrium aluminium perovskite $YAlO_3$ (YAP) is perspective materials for laser engineering and scintillate materials (doped by cerium ions).

The stable color centers (SCC) in pure and doped LNO as well as YAP crystals have been investigated in several works, for example in [4]. The SCC are centers which have lifetime higher than 1 s. Unfortunately, the lifetime of color centers were studied in literature only for transient color centers, for example in [5]. In this work the lifetime of stable additional absorption induced by gamma irradiation in pure and Cu doped LNO as well as Ce doped YAP crystal will be determined from data obtained during 10 years.

2. Experiment

The pure LNO, LNO:Cu (0.05 mol.%) and YAP:Ce (0.3%) crystals were grown from congruent melt in Institute of Electronic Materials Technology (ITME) by the Czochralski technique. Samples for the SCC investigations were made in the form of plane-parallel polished plates of 0.5–1.0 mm thickness. The samples were irradiated with gamma quanta (1.25 MeV) from ^{60}Co with absorbed doses 10^5-10^6 Gy. Optical absorption spectra were recorded with SPECORD-M40 and UNICAM 340 spectrophotometers. The value ΔK of additional absorption induced by external influence was determined as

$$\Delta K = \frac{1}{d}\ln\frac{T_1}{T_2},$$

where d is the sample thickness, T_1 and T_2 are the sample transmission coefficients before and after irradiation, respectively.

The additional absorption (AA) was measured three times: immediately after irradiation (in 2002 year), two years after irradiation and ten years after irradiation.

3. Results and discusions

Absorption spectra of pure LNO crystals immediately after irradiation and before irradiation are given in Fig. 1. The fundamental absorption edge of pure LNO crystal is above 30 000 cm^{-1}, in the region below the crystal is transparent. Irradiation of pure LNO crystals with γ-quanta causes the stable induced absorption (additional absorption, AA) in the 30 000–15 000 cm^{-1} region with two pronounced maxima at 27 000 cm^{-1} and 21 000 cm^{-1} (Fig. 2).

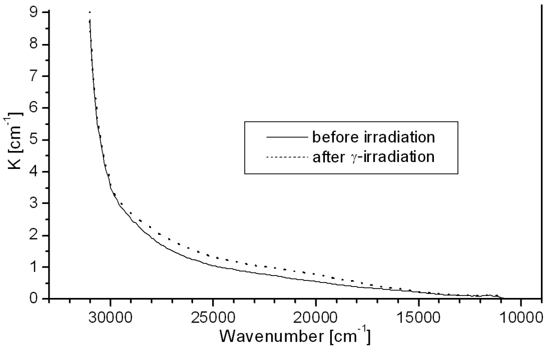

Fig. 1. Absorption spectra of pure LNO crystals immediately after irradiation and before irradiation.

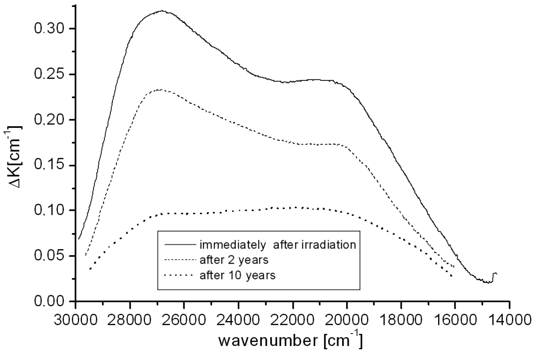

Fig. 2. AA of LNO crystal.

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The absorption band centered at 21 000 cm^{-1} in the LNO crystals after gamma irradiation is attributed to bound small polarons (O^{-} centers stabilized by lattice distortion) and 27 000 cm^{-1} can be due to hole localized into lithium vacancy [6, 7]. According to literature the contribution in AA with maximum near 27 000 cm^{-1} can be also due to O^{-} polarons [8], F^{+} [9] or F [10] centers.

Absorption spectra of LNO:Cu crystals immediately after irradiation and before irradiation are given in Fig. 3. The band imposed on absorption edge centered at 25 000 cm^{-1} is present. This band is associated with the intervalent transition Cu^{+} → Nb^{5+} [11]. The AA spectrum of LNO:Cu crystal after gamma irradiation represents an intensive wide band with maximum near 25 000 cm^{-1} . Besides, some weak clearing near 10 000 cm^{-1} is observed (Fig. 4). Such character of AA spectrum indicates that after the gamma irradiation of LNO:Cu crystals an increasing of the absorption band caused by Cu^{+} ions (at 25 000 cm^{-1}) and decrease of absorption of Cu^{2+} ions (absorbing at 10 000 cm^{-1}) take place [11].

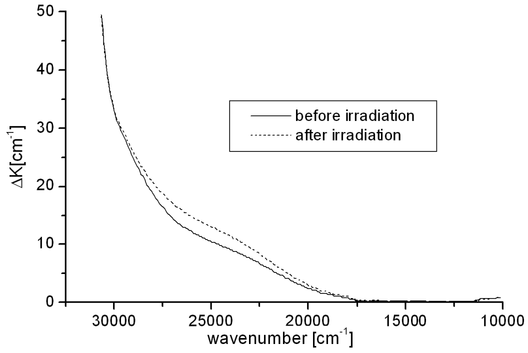

Fig. 3. Absorption spectra of LNO:Cu crystals immediately after irradiation and before irradiation.

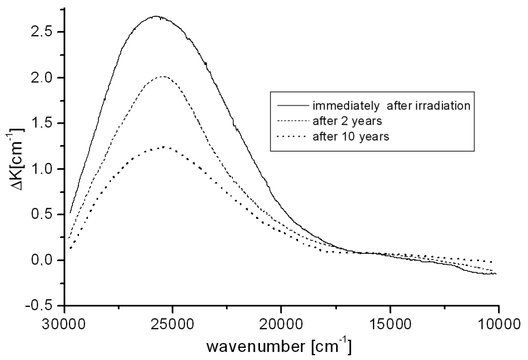

Fig. 4. AA of LNO:Cu.

For YAP:Ce the growth absorption of Ce^{3+} ions was observed after gamma irradiation at new line 34 000 cm^{-1} (Fig. 5). The AA of YAP:Ce present strong intense band centered at 34 000 cm^{-1} (Fig. 6). In YAP:Ce crystals the Ce ions can stay in valence state +3 or +4. This growth of absorption Ce^{3+} ions can be due to electron capture by Ce^{4+} ions [12].

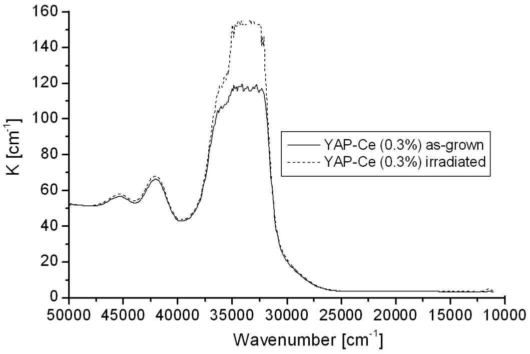

Fig. 5. Absorption spectrum of YAP:Ce before and immediately after irradiation by gamma quanta.

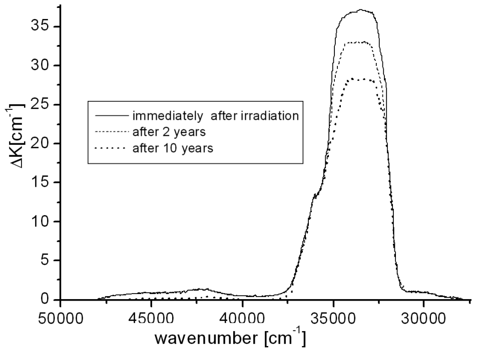

Fig. 6. AA of YAP:Ce crystal.

Decay kinetics for the AA of pure LNO crystal were measured at 27 000 cm^{-1} and 21 000 cm^{-1} and for LNO:Cu crystals at 25 000 cm^{-1} and at 34 000 cm^{-1} for YAP:Ce.

Analysis of decay kinetic for pure LNO at 27 000 cm^{-1} shows that approximation with sum of two exponents is satisfactory. Thus, color centers of two types with substantially different lifetimes contribute to this AA band and decay of AA can be described as:

$$\Delta K(t)_1 = \Delta K_{0,1} + \Delta K_{1,1} \exp\left(\frac{-t}{\tau_{1,1}}\right) + \Delta K_{2,1} \exp\left(\frac{-t}{\tau_{2,1}}\right). \tag{1}$$

where $\Delta K(t)_1$ is the AA value at time t, $\Delta K_{0,1}$ — AA at the time $t \gg \tau_{2,1}$, $\Delta K_{1,1}$ and $\Delta K_{2,1}$ — maximal AA value for the first and second types centers at the beginning of measuring, $\tau_{1,1}$, $\tau_{2,1}$ – lifetimes of the first and second types centers respectively. Numerical values of the equation parameters are listed in Table I. Analysis of decay kinetic for maximum 21 000 cm^{-1} shows that approximation with one exponent is satisfactory

$$\Delta K(t)_2 = \Delta K_{0,2} + \Delta K_{1,2} \exp\left(\frac{-t}{\tau_{1,2}}\right). \tag{2}$$

This means that the maximum at 21 000 cm^{-1} is associated with the centers of one type.

Analysis of decay kinetic for LNO:Cu at 25 000 cm^{-1} shows that approximation with sum of two exponents is satisfactory (Eq. (1)). Thus, also then for pure LNO (at

TABLE I

Decay parameters for AA of LNO crystal.

Parameters	Value
$\Delta K_{0,1}$	0.029 cm^{-1}
$\Delta K_{1,1}$	0.079 cm^{-1}
$\Delta K_{2,1}$	0.212 cm^{-1}
$\tau_{1,1}$	3.49 year
$\tau_{2,1}$	6.57 year
$\Delta K_{0,2}$	0.087 cm^{-1}
$\Delta K_{1,2}$	0.153 cm^{-1}
$\tau_{1,2}$	4.00 year

TABLE II

Decay parameters for AA of LNO:Cu crystal.

Parameters	Value
$\Delta K_{0,1}$	0.67 cm^{-1}
$\Delta K_{1,1}$	0.52 cm^{-1}
$\Delta K_{2,1}$	1.59 cm^{-1}
$\tau_{1,1}$	3.55 year
$\tau_{2,1}$	8.30 year
$\Delta K_{0,2}$	0.03 cm^{-1}
$\Delta K_{1,2}$	0.14 cm^{-1}
$\tau_{1,2}$	9.38 year

27 000 cm^{-1}) centers of two types with different lifetimes contribute to the AA in this maximum. To clarify the nature of centers responsible for absorption at 25 000 cm^{-1} in Cu doped LNO crystal decay kinetic of clearing near 10 000 cm^{-1} have been monitored. Analysis of this decay kinetic show that approximation with one exponent is satisfactory (Eq. (2)). Numerical values of the equation parameters are listed in Table II.

It was clear that $\tau_{2,1}$ is approximately equal to $\tau_{1,2}$ (connected with decay of clearing near 10 000 cm^{-1}). According to [11], the removing of clearing near 10 000 cm^{-1} can be due to growth of concentration of Cu^{2+} according reaction $\text{Cu}^{+} \rightarrow \text{Cu}^{2+} + \text{e}^{-}$. In this way, the $\tau_{2,1}$ is connected with decay of concentration of Cu^{+} ions. Also it is interesting that the $\Delta K_{1,1}$ value is about 3 times smaller than $\Delta K_{2,1}$. This means that a slight contribution to the absorption with maximum 25 000 cm^{-1} may be centers associated with genetic defects and $\tau_{1,1}$ is time decay of stable color centers connected with genetic defects. Should be noted, that $\tau_{1,1}$ in LNO:Cu (3.55 year) is near equal to “short-life” centers in LNO (3.49 year) and that “long-life” centers that occur in pure LNO ($\tau_{2,1} = 6.57$ year) not appear in LNO:Cu.

Analysis of decay kinetic for YAP:Ce shows that approximation with one exponent is satisfactory (Eq. (2)). Numerical values of the equation parameters are listed in Table III.

TABLE III

Decay parameters for AA of YAP:Ce crystal.

Parameters	Value
$\Delta K_{0,2}$	26.47 cm^{-1}
$\Delta K_{1,2}$	11.29 cm^{-1}
$\tau_{1,2}$	3.92 year

The decay of absorption Ce^{3+} ions can be due to electron release, according reaction $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + \text{e}^{-}$, as opposite process then during gamma irradiation.

4. Conclusion

The stability of stable color centers connected with genetic defects in LNO and LNO:Cu crystals are smaller than seven years. In pure LNO “short-life” centers and that “long-life” centers (with half time near twice as large as “short-life” centers) were observed. The stability of Cu^{+} ions in LNO:Cu is near 8 years and Ce^{3+} in YAP:Ce is about 4 years.

Acknowledgments

Thank you very much to Prof. T. Lukasiewicz for sample preparation and Dr. D.Yu. Sugak for sample irradiation.

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