



Electron paramagnetic resonance study of impurities and point defects in oxide crystals

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ABSTRACT

In this topic review the results of the X-band electron paramagnetic resonance (EPR) measurements of Mn, Co, Cr, Fe ions in YAlO₃ (YAP) crystals and Fe ions in LiNbO₃ (LNO) crystals and of chromium doped Bi₁₂GeO₂₀ (BGO) and Ca₄GdO(BO₃)₃ single crystals, are presented. It is well known that the oxide crystals (for example: YAP, LNO, BGO) are one of the most widely used host materials for different optoelectronic applications. The nature of point defect of impurities and produced in the oxide crystal after irradiation by bismuth ions and after irradiation by the ²³⁵U ions with energy 9.47 MeV/u and fluency $5 \times 10^{11} \text{ cm}^{-1}$ is discussed. The latter is important for applications of these oxide crystal as laser materials.

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1. Introduction

The oxide crystals (for example: YAP, LNO, BGO) are one of the most widely used host

materials for different optoelectronic applications. The most known use of these crystals are laser materials. In this respect, it is particularly important to know the nature of defects. It is preferred for this purpose to produce artificial defects in the above named materials and to examine them by so precise method which is Electron Paramagnetic Resonance (EPR). It is advantageous to briefly describe some of the most important oxide crystals for approximations' background and formulation of research questions.

Yttrium orthoaluminate crystals (YAlO₃ or YAP) are one of the most important materials for solid-state lasers. Recently, some new interesting properties of Mn-doped YAlO₃ have been reported, among them strong photochromic effect [1] and intensive thermally stimulated luminescence (TL) after γ –irradiation [2]. Manganese ions in YAlO₃:Mn crystals as a rule are present in a form of Mn⁴⁺ ions in the octahedral coordination (Al³⁺ positions) and Mn²⁺ ions in the strongly distorted dodecahedral coordination (Y³⁺ positions) [1,3–6]. Crystals being exposed to a blue-green laser light show an intensive bluish-gray coloration caused by Mn⁵⁺ ions created as a result of the Mn⁴⁺ → Mn⁵⁺ + e[−] photoionization process [1,3]. In such a way, the Mn⁴⁺ ions demonstrate sensitivity to the visible light exposure. The Mn²⁺ ions are sensitive to the ionizing radiation such as X- or γ –rays, as well as UV radiation [7]. Explanation of this effects is required. Yttrium aluminum perovskite YAlO₃ crystals doped with rare-earth ions (Nd³⁺, Tm³⁺, Er³⁺) belong to the most important solid state laser materials [8,9], as well as they are also promising materials for scintillators (YAP:Ce) [10], and as substrates for thin films' epitaxy [11]. Co-doped oxide crystals are attractive materials for 'eye safe' laser operation near 1.5 μ m and as nonlinear absorbers for passive Q-switching [11,12]. EPR and optical spectra, as well as nonlinear absorption properties of Y₃Al₅O₁₂:Co, SrLaAlO₄:Co, Mg₂Al₂O₄:Co, LaGaO₃:Co, and SrLaGa₃O₇:Co were investigated in Refs. 12–16. The EPR spectra of various ions in YAlO₃ crystals, e.g. the 3dN ions Cr³⁺, Ti³⁺, Mn⁴⁺, Mn⁵⁺ and Fe³⁺ [3,17–20] and the 4fN ions Er³⁺, Nd³⁺ and Ce³⁺ [21–23], were also previously studied [24–28]. An in-depth analysis of these studies is desirable.

Lithium niobate (LiNbO₃) is a ferroelectric material which does not occur naturally. Due to its physical and chemical properties LiNbO₃ is an important material for many applications [29,30]. LiNbO₃ crystal is of sustained scientific and technical interest, mainly due to its desirable ferroelectric, piezoelectric, and photoelectric properties [31,32], even for acoustical memory as recently reported [31]. The most extensive application is the ferroelectric property which mainly originates from the structure distortion in LiNbO₃ itself, i.e. the Li⁺ and Nb⁵⁺ cations move away from their position in the paraelectric phase [33].

However, the reported values of the spin-Hamiltonian (SH) parameters obtained from EPR of Fe³⁺ in LiNbO₃ are not uniform because of different experimental conditions and crystal composition [34–36]. It is necessary to systematize and complement previous studies.

Germanosilicite Bi₁₂GeO₂₀ (BGO) as well as Bi₁₂SiO₂₀ (BSO) crystals have been widely used in photorefractive, photoconductive, electro-optical and acousto-optical applications including two-wave mixing, four-wave mixing, phase conjugation, real-time holography, optical data storage, optical computing, electro-optical modulation, thin film optical waveguides [37–40].

Optical and photochromic properties of BGO:Cr crystals were early connected with chromium ions located in the Ge⁴⁺ tetrahedral positions [41,42]. The chromium ions in BGO:Cr can be in Cr⁴⁺ and Cr⁵⁺ state [41,42]. The EPR spectra of Cr ions in BGO crystals were

also previously studied [43] and in-depth analysis of these studies is desirable also.

Rare earth (RE) doped gadolinium calcium oxoborate Ca₄GdO(BO₃)₃ (GdCOB) crystals attract significant interest of researchers, since they are promising materials for bi-functional lasers and non-linear optical transformations [44,45]. Their possible applications are: colour displays, data storage devices, medical diagnostic, quantum electronics and optoelectronic materials. A possibility of effective doping the GdCOB crystal by different RE ions was demonstrated in Refs. 46,47. Incorporation of RE elements leads to an enhancement of the non-linear optical coefficient, improvement of emission efficiency, phase matching and technological conditions. EPR study of these centres are promising and important.

The aim of this review paper is to complete characteristics of impurities presented in selected oxide crystals as indicated by EPR measurements. For this purpose, the spin Hamiltonian analysis of EPR spectra has been carried out on the basis of the triclinic (C₁) site symmetry. Comparison of examined defects in different crystals enable us to find optimal conditions in order to improve the properties of the laser materials.

2. Crystal structure of investigated materials

The crystal structure of materials studied by EPR is critical for in-depth analysis of experimental data. There are also the exact characteristics required in the first place.

2.1. Yttrium orthoaluminate crystals

The structural data indicate that YAP crystallizes in an orthorhombically distorted perovskite structure with the lattice parameters a = 0.518 nm, b = 0.533 nm, c = 0.737 nm [4,48,49]. The space group D_{2h}¹⁶ was chosen to describe the symmetry of the unit cell in YAP crystals using the Pbnm group coordinate system [48,49]. The structure of YAlO₃ can be represented (see Fig. 1) as a grid of tilted AlO₆ octahedra with the Y ions occupying the empty space between the octahedra. The ionic radii of the cations, R, are R(Y³⁺) = 0.097 nm, R(Al³⁺) = 0.057 nm, R(Co³⁺) = 0.064 nm, R(Co²⁺) = 0.078 nm, R(Nd³⁺) = 0.099 nm and R(Er³⁺) = 0.085 nm [50]. The O–Al–O angles in the respective octahedra vary in the range 89.6°–90.6°.

Since deviations of the respective angles from 90° and the bond-length distortion are small, the AlO₆ octahedra may be considered to be only slightly distorted. The immediate surrounding of the Y cations consists of eight oxygen anions, whereas the Y–O bond-lengths in the YO₈ dodecahedra differ one from another, e.g. in the range from 0.2284 to 0.2597 nm for YAP–1% Nd. Hence, the YO₈ dodecahedra are considerably distorted with a bond-length distortion equal to 0.315 nm [4].

2.2. Lithium niobate

At room temperature, the space group in the ferroelectric phase is R3c with the hexagonal unit cell of a_H = 0.515 nm and c_H = 1.386 nm (Fig. 2). Below T_c (= 1145 °C) the C₃ symmetry is characterized by a displacement of the cations (Li⁺ and Nb⁵⁺) along the crystallographic c-axis [51,52].

Due to the displacement of the cations, both ions reside in oxygen octahedra with small distortion. The stacking order of the octahedral sites along the c-axis becomes Li, Nb, structural vacancy (Vs), Li, Nb, Vs and so on. In the paraelectric phase, the point group of the material is C_{3v} [51,52]. The oxygen layers are equally spaced along the c-axis. For the Li⁺, Nb⁵⁺ and Fe³⁺ ions, the electro-

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