

# Temperature Dependence of $Mn^{2+}$ Paramagnetic Ion in a Stoichiometric $LiNbO_3$ Single Crystal

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**Electron paramagnetic resonance (EPR) spectra of  $Mn^{2+}$  impurity ion in stoichiometric  $LiNbO_3$  single crystal (SLN) was investigated with an X-band EPR spectrometer in the temperature range of 3 K–296 K. The intensity of EPR spectrum of  $Mn^{2+}$  ion was increased to 20 K and decreased again below 20 K as the temperature decreases. The zero-field splitting parameter  $D$  decreased as the temperature increases. It was suggested that  $Mn^{2+}$  ion substitute for  $Nb^{5+}$  ion instead of  $Li^+$  ion. No changes for hyperfine interaction of  $Mn^{2+}$  ion was obtained in the temperature range of 3 K–296 K.**

**Keywords:**  $LiNbO_3$  single crystal,  $Mn^{2+}$  ion, electron paramagnetic resonance, temperature dependence

## 1. Introduction

Lithium niobate ( $LiNbO_3$ ) is a typical non-stoichiometric material, and is usually grown by the Czochralski method from a congruent melt.  $LiNbO_3$  single crystal has been widely used due to its ferroelectric, piezoelectric, photoelectric properties, holographic volume storage, coherent optical amplification, and phase conjugation [1-7]. However, the congruent  $LiNbO_3$  (CLN) crystals used usually contained a considerably large amount of intrinsic defects due to Li deficiency, which lead to the long response times, low refractive index changes and low sensitivities. These large amounts of intrinsic defect greatly degrades the applications of  $LiNbO_3$  crystals [8, 9].

The photorefractive properties of un-doped CLN crystals are often relatively poor.  $LiNbO_3$  crystals doped with transition metal ion Cu, Fe, Mn, Ce etc., exhibit significant photorefractive properties and are potential material for holographic memories [10-12]. The photorefractive effect, which is used for the storage of volume phase holograms, is due to the presence of transition metal impurities and intrinsic lattice defects [13]. Both the photorefractivity and quality of holography depend on the presence of defects generated during growth as well as deliberately added impurities, usually the transition metal

ions. The incorporation of active ions allows the fabrication of photonic devices such as integrated lasers and amplifiers [14]. Doping with damage-resistant dopants is also found to be an effective method that increases the optical damage resistance [15].

Recently, the stoichiometric  $LiNbO_3$  (SLN) crystal has attracted much attention for its improvements in many physical properties as compared with CLN crystal [16-20]. The SLN crystals show larger electro-optical and nonlinear effects than those of the CLN crystals [21]. In addition, the coercive fields of the SLN crystals have been reported to be much lower, approximately one-fifth of the CLN crystals at room temperature [22]. Increasing the  $[Li]/[Nb]$  ratio in  $LiNbO_3$  can also reduce the intrinsic defect concentrations greatly, and thus, the response time can be shortened to the order of seconds in stoichiometric crystals [23].

Since the impurity and defect can strongly influence the electric, optical and magnetic properties of  $LiNbO_3$  crystal, the spectroscopy studies of  $LiNbO_3$  including impurity and defect have gained considerable interests [24-27]. The local site symmetry, the substituted position and ionic state of the optically active ions in  $LiNbO_3$  crystal can be determined by EPR techniques [28]. A number of NMR [29] and EPR [30-33] studies have been performed on  $Mn^{2+}$  doped  $LiNbO_3$  crystals. In this study, the EPR study of  $Mn^{2+}$  ion in stoichiometric  $LiNbO_3$  single crystal has been investigated as a function of temperature. The temperature dependence of zero-field splitting parameter and

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intensity of Mn<sup>2+</sup> spectra are analyzed to find the substituted site location of Mn<sup>2+</sup> impurity ion in the host material.

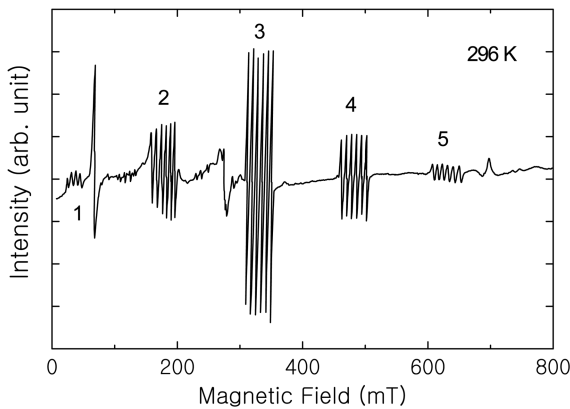
## 2. Crystal Structure and Experiments

The unit cell of LiNbO<sub>3</sub> is rhombohedral with the lattice constants at room temperature,  $a = 0.514739$  nm and  $c = 1.385614$  nm [34]. The space group of LiNbO<sub>3</sub> belongs to R3c (C<sub>3v</sub><sup>6</sup>) [35]. The LiNbO<sub>3</sub> structure is build of oxygen atoms arranged in planar sheets which form chains of trigonally distorted octahedral, adjoined by walls, spreading along the crystallographic c-axis. The sequence of octahedral repeats [Nb, vacancy, Li] along the c-axis, so 1/3 amount of the octahedral is empty [34, 35].

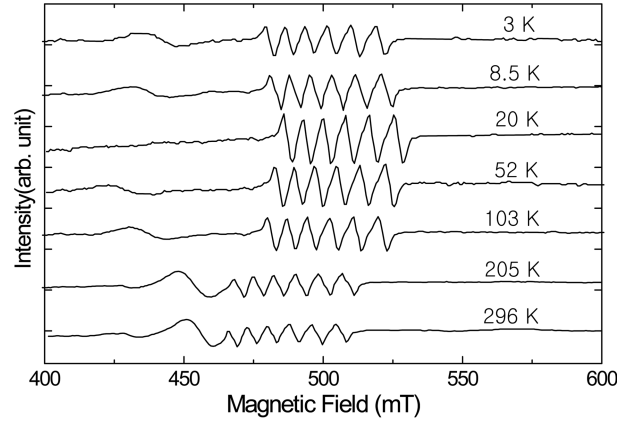
The impurity ions may occupy one of the three octahedral sites (Nb<sup>5+</sup>, vacant octahedron, Li<sup>+</sup>). The LiNbO<sub>3</sub> contains several defects including anti-site defects (Nb<sup>5+</sup> ion in a Li<sup>+</sup> site, namely Nb<sub>Li</sub>) and three octahedral sites. All paramagnetic sites positioned along the c-axis of LiNbO<sub>3</sub> crystal have the C<sub>3</sub> point group symmetry, while the impurity ions at other positions have the lowest C<sub>1</sub> symmetry [36].

An X-band Jeol EPR spectrometer was employed to record the Mn<sup>2+</sup> spectra in SLN single crystal. Fig. 1 shows a typical EPR spectrum of Mn<sup>2+</sup> ion at room temperature when magnetic field B is applied to the crystallographic c-axis. The five groups of lines labeled 1, 2, 3, 4, 5 are the fine structures of Mn<sup>2+</sup> (S = 5/2), and the six lines within each group are the hyperfine structures of <sup>55</sup>Mn (I = 5/2, 100% abundance).

To examine the temperature dependence of EPR parameters for the Mn<sup>2+</sup> ion in a SLN single crystal, the resonance spectra were measured at different temperatures in the range 3–296 K. Fig. 2 shows the temperature



**Fig. 1.** Typical EPR spectra of Mn<sup>2+</sup> ion in stoichiometric LiNbO<sub>3</sub> single crystal when magnetic field B is applied to the crystallographic c-axis.



**Fig. 2.** Temperature dependence of Mn<sup>2+</sup> ion in stoichiometric LiNbO<sub>3</sub> single crystal when magnetic field B is applied to the crystallographic a-axis.

dependence of Mn<sup>2+</sup> ion at seven different temperatures when magnetic field B is applied to the crystallographic a-axis. The peak-to-peak intensity of Mn<sup>2+</sup> EPR lines increases approximately linearly with decreasing temperatures from RT to 20 K and reaches a maximum at a temperature of 20 K. Below the 20 K, however, the peak-to-peak intensity decreases.

## 3. Analysis

The Mn<sup>2+</sup> ion has the electron configuration 3d<sup>5</sup> and is an S-state ion with S = 5/2 and a basic level of <sup>6</sup>S<sub>5/2</sub>. When this ion is embedded in a SLN crystal, it experiences an intense crystal field produced by the neighboring ions because the 3d shell of the Mn<sup>2+</sup> ion is the outmost one. Consequently, fine structure arises from the crystal field, and the spin-spin interaction and the hyperfine structure results from the interaction between the nuclear spin of <sup>55</sup>Mn and its electronic spin. Accordingly, the experimental results for the resonance fields can be analyzed with the usual spin Hamiltonian [37]

$$H = H_Z + H_{zfs} + H_h \quad (1)$$

where the terms on the right-hand side are the Zeeman interaction, the fine structure (zero-field splitting) and the hyperfine interaction, respectively. The Zero-field splitting term is

$$H_{zfs} = \sum B_k^q O_k^q \quad (2)$$

where  $O_k^q$  is the extended Stevens operators [38]. The relation between the conventional and Stevens notations is  $D = 3B_2^0$  [37]. The hyperfine interaction is

$$H_h = S \cdot A \cdot I \quad (3)$$

where  $A$  represents the hyperfine tensor.  $S$  and  $I$  are the electron and nuclear spin vectors, respectively.

The peak-to-peak intensity of  $Mn^{2+}$  EPR line increases almost linearly with decreasing temperatures from RT to 20 K as can be seen Figure 2. When an external magnetic field is applied, magnetization is inversely proportional to the temperature from the Curie law. Therefore, it is reasonable that the intensity of resonance line for  $Mn^{2+}$  paramagnetic impurity ion increases as the temperature decreases because magnetic moments of  $Mn^{2+}$  ion seem to align as the temperature decreases. However, the intensity of  $Mn^{2+}$  EPR line reaches a maximum at a temperature of 20 K and decreases below the 20 K. It seems that the alignments of magnetic moments of  $Mn^{2+}$  ion is frustrated under 20 K. Therefore, the intensity of  $Mn^{2+}$  resonance line decreases below 20 K. The geometrical magnetic frustrations are studied in amorphous materials, glasses, or dilute magnets, which is a state exhibiting magnetic frustration at low temperatures. The Ho-, Dy-, and Gd-based double perovskites show the characteristics of geometric magnetic frustration at low temperatures [39].

The ZFS parameter  $D$  of  $Mn^{2+}$  center can be calculated from the effective spin Hamiltonian Eqs. (1) and (2). The  $D$  value was already calculated in many previous papers [30-33]. Only the variation of  $D$  values as a function of temperature for  $Mn^{2+}$  ion is interested in this study. It is found that the  $D$  value decreases as the temperature increases above 20 K which can be easily seen in Fig. 2.

The crystal field is proportional to the nuclear quadrupole coupling constant  $e^2qQ/h$  [40]. The ZFS can be changed according to the crystal field. Thus, it may acceptable that ZFS parameter  $D$  is proportional to  $e^2qQ/h$  when there is some proportionality between CF and ZFS. There is also formal similarity, not physical similarity, between  $D$  and  $e^2qQ/h$  in EPR and nuclear magnetic resonance (NMR) Hamiltonian [41]. Since  $Mn^{2+}$  is spherically symmetric, the electric field gradient (EFG) is directly related to the crystal field parameter [42]. According to the previous EPR measurements,  $Mn^{2+}$  ion is located at the site of crystallographic  $C_3$ -axis [33]. As the temperature increases, the  $e^2qQ/h$  of  $Li^+$  in  $LiNbO_3$  increases, whereas  $e^2qQ/h$  of  $Nb^{5+}$  and  $D$  of  $Mn^{2+}$  decrease. As the temperature increases, the Nb ions move to the center direction of the inversion so as to occupy a position between the oxygen layers; on the other hand, the Li ions move away from the center of inversion so as to occupy a position in the plane of oxygen layers. When considering the axial components, the crystal field action on the  $Nb^{5+}$  decreases and increases at the Li site (if the nearest oxygen ions are considered) [30]. Therefore, from the comparison of temper-

ature dependence between  $e^2qQ/h$  and  $D$ , we can conclude that  $Mn^{2+}$  impurity ion replaces  $Nb^{5+}$  ion instead of  $Li^+$  ion in SLN.

The hyperfine interaction of  $Mn^{2+}$  paramagnetic impurity ion is obtained from the effective spin Hamiltonian Eqs. (1) and (3). The hyperfine constant  $|A|$  was obtained by a first-order perturbation to the Zeeman term because the hyperfine interaction turns out to be much smaller than the Zeeman. The hyperfine constant of  $Mn^{2+}$  ion was found to be  $|A| = 78.5 \text{ G} \pm 1.5 \text{ G}$  which is constant within experimental accuracy of the temperature range 3~296 K.

## 4. Results

The temperature dependence of  $Mn^{2+}$  paramagnetic impurity ion in stoichiometric  $LiNbO_3$  single crystal has been investigated by EPR spectrometer. The peak-to-peak intensity of  $Mn^{2+}$  resonance line increases as the temperature decreases which is consistent with Curie law. The intensity of  $Mn^{2+}$  paramagnetic ion was decreased from the magnetic frustration at low temperatures. The zero-field splitting parameter decreases as the temperature increases. It was suggested that the  $Mn^{2+}$  impurity ion substitutes for the  $Nb^{5+}$  ion instead of  $Li^+$  ion in stoichiometric  $LiNbO_3$  single crystal when comparing the temperature dependences between the ZFS parameter and crystal field. The hyperfine splitting of  $Mn^{2+}$  ion in SLN does not change as the temperature changes from 3~296 K.

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