Doping Effects of Mg and/or Fe ions on

Congruent LiNbO$_3$ Single Crystal Growth

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Abstract

The doping effects of Mg and/or Fe ions on congruent LiNbO$_3$ single crystal growth were studied in order to clarify the roles of MgO in Fe doped LiNbO$_3$ single crystals. The effective distribution coefficient of Fe was found decreased drastically from 0.85 to 0.5 by the addition of MgO into the LiNbO$_3$ melt. Mössbauer spectra revealed that the addition of MgO reduces the occurrence of Fe^{2+} ions during growth in air. Therefore, it is likely that there would be two important roles of MgO in Fe doped LiNbO$_3$. One is to suppress the incorporation of all Fe ions, and the other is to reduce the concentration of Fe^{2+} ions among the total Fe ions.

1. Introduction

LiNbO$_3$ (LN) crystal is one of the most extensively used ferroelectric materials. However, its use in optoelectronic devices such as light modulators, deflectors, and frequency doublers has been severely limited by low optical damage threshold [1-3].

It has been known [1-4] that the beneficial dopants for the suppression of the optical damage are Mg, Zn, Sc, In; on the contrary, the harmful dopants are Fe, Mn, and Cu. The typical example is addition of 4 or 5 mol% MgO. However, regarding the reason why MgO suppresses the optical damage so remarkably is not clearly explained yet.

In this study, the doping effects of Mg and /or Fe ions on LN melt was investigated in

order to clarify the roles of MgO in Fe doped LN crystal. Some results were discussed in terms of competition between two ions during growth (codoping effect). Mössbauer measurements were also carried out for the examination of charge state of Fe ions.

2. Experimental Procedure

The starting materials were prepared by mixing Li_2CO_3 and Nb_2O_5 powders at a congruent ratio of Li: Nb = 48.5 : 51.5 (mol%) , and doped with MgO and/or Fe_2O_3. Dopant concentrations of MgO and Fe_2O_3 were 5 mol% and 0.5 mol%, respectively. The crystals were grown along c-axis in air using platinum crucibles by Czochralski method. All grown crystals were about 18 mm in diameter. Mg and Fe concentrations in the grown crystals were determined by EPMA. X-ray powder analyses with Cu $K\alpha_1$ radiation were done for phase identification and lattice constants determination. The optical absorption spectra were measured by an UV spectrometer in the wave length range of 200-700 nm. ^{57}Fe Mössbauer spectra were studied at room temperature with a conventional constant acceleration spectrometer for Fe and Mg+Fe codoped samples which were as-grown or annealed in Ar.

3. Results and Discussion

Fig. 1 shows the variations of dopant concentrations measured by EPMA along the growth axis as a function of solidification fraction, g. The concentration is described by the equation $C_s / C_o = k_{eff}(1-g)^{k_{eff}-1}$, where k_{eff} is the effective distribution coefficient, C_s and C_o are dopant concentrations in the crystal and in the melt, respectively. It is apparent that the
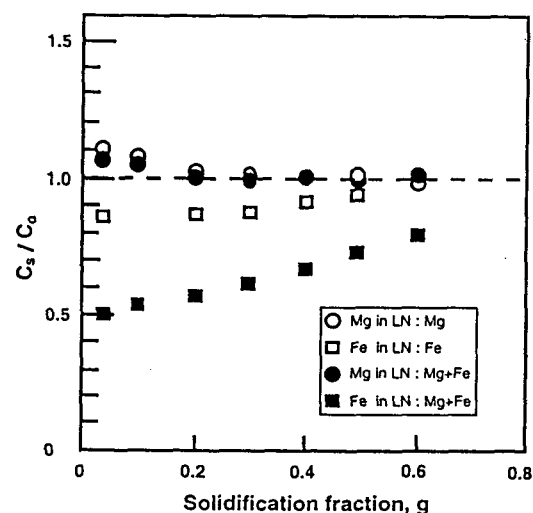

Fig. 1

Fe concentration is decreased remarkably from 0.85 to 0.5 when the crystal was codoped with Mg ions. However, Mg concentration was almost unchanged whether doped singly or codopedly with Fe ions. Hence, it is clear that MgO decreases the incorporation of Fe ions into LN.

Fig. 2 shows the optical absorption spectra measured for the crystals grown. The broad absorption peak appeared with maximum around 480 nm by Fe doping, and this shape was not affected by Mg addition. It demonstrates that some Fe^{2+} ions are existing, and that the optical absorption of LN is strongly dependent on the Fe amount rather than Mg concentration

Fig. 2

Fig. 3 shows the M ö ssbauer spectra of various LN single crystals measured at room temperature. Since the absorption peak at v =1.9 mm/s is a signal exclusively from Fe^{2+}, the behaviour of Fe^{2+} can be estimated by this peak [5]. It reveals that the addition of MgO in LN slightly can decrease Fe^{2+} ions during crystal growth in air, however, can not prevent the increase of Fe^{2+} ions during annealing in Ar.
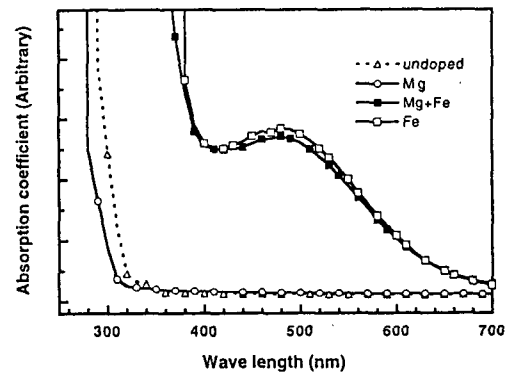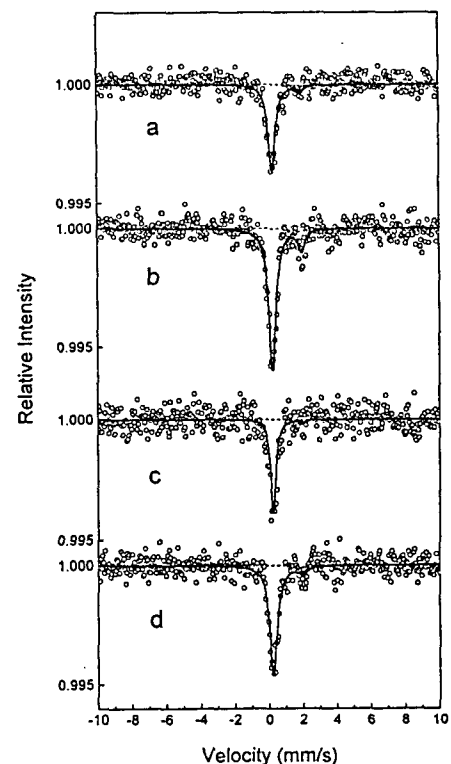

Fig. 3.
(a) as-grown state of Fe, (b) after annealed state of Fe , (c) as-grown state of (Mg+Fe), (d)After annealed state of (Mg+Fe)

The change of the distribution coefficient of Fe by the addition of MgO into Fe doped LN

suggests that there is a competition between two ions during crystal growth. The incorporation or distribution coefficient of a dopant is closely correlated with sites where it prefer to occupying [6]. The site competition during crystal growth would arise because of different distribution coefficients of dopants when they participate the same sites (Li sites). Since more preferable Mg ions are occupied Li sites with maximal incorporation rate, the possibility of incorporation of Fe ions to Li sites are reduced. Total amounts of LN positions are determined by LN structure. Thus, the amount of Li sites which could be substituted by dopants is limited also. As a result, there would be incorporation of Fe ions for the remained sites only after Li sites are firstly occupied by Mg ions. When the remained sites are deficient compare to the doping amounts of Fe ions, some part of Fe ions, which can not incorporate in LN crystal, is rejected by the structure.

4. Conclusion

The behaviors of Mg and/or Fe doped LN were studied. The distribution coefficient of Fe was remarkably reduced by the addition of MgO in the LN melt. Therefore, It is clear that MgO suppresses the incorporation of Fe ions during crystal growth. It may be due to a site competition between Mg and Fe ions in the melt; thereby, more preferable Mg ions prevent the incorporation of Fe ions during crystal growth. The addition of MgO reduces the incorporation of Fe^{2+} ions during crystal growth in air, which was confirmed by Mössbauer spectra.

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