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# The effect of native defects on the domain structures of $\text{LiNbO}_3\text{:Fe}$ —a case study by means of the addition of $\text{MgO}$ and $\text{K}_2\text{O}$ to the congruent melt

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**Abstract.** The effect of native defects on the domain structure of  $\text{LiNbO}_3\text{:Fe}$  has been investigated. To reduce the number of native defects, two methodologies have been adopted: firstly, co-doping with Mg; and secondly, the addition of  $\text{K}_2\text{O}$  to the congruent melt. When grown from congruent melts,  $\text{LiNbO}_3\text{:Fe}$  has a multi-domain nature. Co-doping with Mg changes the domain structure, although the crystals are still multi-domain. On addition of  $\text{K}_2\text{O}$ , single-domain crystals are obtained. The change in domain structure brought about by doping with Mg is due to compensation of the stoichiometric defects. On the other hand, reduction in the number of intrinsic defects due to change in the Li/Nb ratio in the crystal as a result of the addition of  $\text{K}_2\text{O}$  to the melt is responsible for the mono-domain structure.

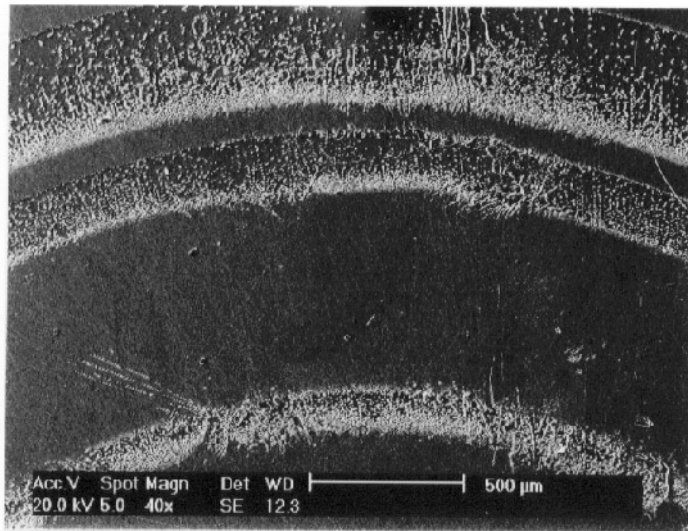
## 1. Introduction

Lithium niobate doped with iron ( $\text{LiNbO}_3\text{:Fe}$ ) has been extensively used in studying the photorefractive effect and its applications [1–6]. Usually the concentration of Fe, which is in the range 0.01 to 0.1 wt% in the crystal, is masked by the high concentration of stoichiometric defects [7, 8], such as lithium vacancies, and complex defects comprising niobium antisites and niobium vacancies, in  $\text{LiNbO}_3$  ( $V_{\text{Li}}'$ ,  $\text{Nb}_{\text{Li}}^{\dots}$ ,  $V_{\text{Nb}}^{\dots}$ , respectively, following the standard Kroger–Vink notation) grown from a pure congruent melt. Thus the actual influence of Fe on the defect structure of  $\text{LiNbO}_3$  is difficult to investigate. To circumvent this problem, either Mg [9] or Zn [10] doping is carried out, which will reduce the intrinsic defect concentration in the crystal by compensation. However, the impurity contents of Mg and Zn are often so large that their effect outweighs the effect of the Fe. Recently, Malovichko *et al* [11–14] have been able to grow stoichiometric crystals of  $\text{LiNbO}_3$  from a congruent melt containing 6 wt% of  $\text{K}_2\text{O}$ , and papers have been published that clarify the differences between stoichiometric and congruent crystals [15, 16]. The latter approach was subsequently used for studying the effect of Fe on the defect structure of  $\text{LiNbO}_3$ .

The aim of the present investigation was to study the effect of the change in crystal composition on the domain structure in as-grown  $\text{LiNbO}_3\text{:Fe}$ . A comparison has been made with the case in which  $\text{MgO}$  is co-doped in the crystal together with Fe. From the practical point of view, obtaining a single-domain crystal is an essential criterion for any

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applications. Usually, post-growth poling is employed for poling the crystals to a mono-domain form. However, this may lead to a redistribution of the impurities, induced by the electric field at high temperatures during the poling. The domain repolarization, and thus its distribution and nature, can also be varied by impurity and thermal gradients, even when not using the conventional electric field method [17]. The present study was also aimed at identifying the most favourable growth conditions for obtaining mono-domain crystals without the application of any external field.



**Figure 1.** Typical domain structure in a  $\text{LiNbO}_3\text{:Fe}$  crystal grown from a congruent melt.

## 2. Experimental details

The details of the experimental set-up used for the crystal growth, and the conditions imposed to control the diameter are described elsewhere [18]. Crystals with diameter 20 mm and length 75 mm were grown by employing a rotation rate of 30 rpm and a pulling rate of  $2.3 \text{ mm h}^{-1}$  in the cases of growth from a congruent melt, and  $0.5 \text{ mm h}^{-1}$  in the cases of addition of  $\text{K}_2\text{O}$  to the congruent melt. The melt was contained in a Pt crucible, and consisted of congruent compositions of  $\text{LiNbO}_3$  and  $\text{Fe}_2\text{O}_3$  with the addition of  $\text{K}_2\text{O}$  or  $\text{MgO}$ . The  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$  contents in the melt were 0.1, 2, and 9.5 mol% respectively. Seeds with orientation along the  $c$ -axis were used. The seeds were multi-domain in nature, obtained from crystals grown previously using congruent melts. After the termination of the growth experiments, the crystals were sliced perpendicularly to the growth direction (the  $c$ -axis), mechanically polished with Buehler alumina powder with a  $0.5 \mu\text{m}$  mesh, and etched in  $\text{HF:HNO}_3$  (1:2) at  $110^\circ\text{C}$  for 10 min to reveal the domain structure in the wafers. A Zeiss optical microscope or a scanning electron microscope (SEM) was used to observe the domain pattern in the wafers. Optical absorption measurements to determine the composition of the crystals were carried out at room temperature using a commercial Hitachi U-3501 spectrometer with a spectral sensitivity of 0.1 nm.

### 3. Results and discussion

The optical absorption spectra of the crystals grown from the congruent melt with MgO doping clearly indicated the non-stoichiometric nature of the crystals. On the other hand, the crystals grown using a congruent melt with the addition of  $\text{K}_2\text{O}$  exhibited a near-stoichiometric composition. The absorption edge position, defined as the wavelength at which the absorption coefficient is  $20 \text{ cm}^{-1}$  at 295 K, is 310.5 nm for the near-stoichiometric crystals and 320 nm for the congruent crystals. In the former case, the discrepancy between this result for the absorption edge and the extrapolated data of Malovichko *et al* [12] is probably due to the real composition in the crystal. Further work on these kinds of crystal is under way [19].

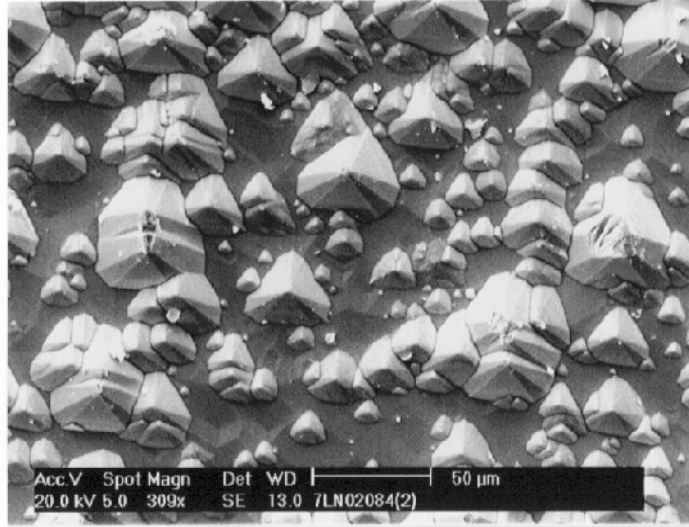
Figure 1 shows a typical domain structure in the crystals grown from a congruent melt with  $\text{Fe}_2\text{O}_3$  addition. The multi-domain nature, with concentric rings, can be seen throughout the wafer. This is similar to the domain structure in undoped pure  $\text{LiNbO}_3$  grown from a congruent melt. This implies that the doping of the melt with Fe does not induce any significant changes in the domain structure in  $\text{LiNbO}_3$ .



**Figure 2.** Domain structure in MgO-co-doped  $\text{LiNbO}_3:\text{Fe}$  grown from a congruent melt.

The domain structure in the MgO-co-doped  $\text{LiNbO}_3:\text{Fe}$  samples remains poly-domain in our experiments, although previous studies [20] show a single-domain nature of the crystals. The difference between the domain structures of  $\text{LiNbO}_3:\text{Fe}$  and  $\text{LiNbO}_3:\text{Mg}:\text{Fe}$  crystals lies in the pattern of the hillocks, as is shown in figure 2. The multi-domain nature exhibited by our samples may be due to low levels of MgO in the melt. High doping levels may be necessary to convert the multi-domain nature to a completely single-domain nature.

The iron-doped crystals grown from congruent melts with  $\text{K}_2\text{O}$  addition exhibited single-domain nature irrespective of the domain structure of the seed. Typical etch hillocks on the negative domain are shown in figure 3. It is known from previous studies that there is no incorporation of potassium in the crystal. On the other hand, addition of  $\text{K}_2\text{O}$  helps in obtaining the stoichiometric composition of the crystals. Thus it is obvious that the change in domain structure is due to the variation of the composition in the crystal.



**Figure 3.** Typical etch hillocks on the negative domain of a mono-domain  $\text{LiNbO}_3\text{:Fe}$  sample grown from a congruent melt containing  $\text{K}_2\text{O}$ .

From the present study, it can be concluded that the domain structure in  $\text{LiNbO}_3$  depends on the native defect concentration. Reduction of the number of stoichiometric defects enhances the probability of obtaining mono-domain crystals during growth, even without application of an electric field, and using multi-domain seeds. By either compensating the native defects by co-doping above a certain limit (of  $\text{MgO}$ ) or by decreasing the intrinsic concentration by addition of  $\text{K}_2\text{O}$  to the melt, one can obtain mono-domain crystals. This point is extremely important for practical applications, as applying an external field to the crystal has its own disadvantages and problems. It may be argued that in the case of the growth using a  $\text{K}_2\text{O}$ -containing melt, the crystal growth temperature as determined from the phase diagram [21] is below the Curie temperature, and hence one should always expect a single-domain nature. However, extensive experiments using  $\text{K}_2\text{O}$  melts, and transition metal and rare-earth dopants with the same growth conditions, have shown that this is not the case. For example, Hf- or Er-doped  $\text{LiNbO}_3$  (1 mol% Hf and 0.05 mol% Er) grown from a congruent melt containing  $\text{K}_2\text{O}$  exhibit a poly-domain nature even though the growth temperature is below the Curie transition. The structure of defect complexes in the final crystal could play a significant role in determining the domain structure. This topic is under investigation, and will be reported on later, elsewhere. It is perhaps worth mentioning that recent work by Malovichko *et al* [22] has shown that introduction of  $\text{MgO}$  in a high concentration (more than 6 mol.%) lowers the concentration of Li in the crystal via both substitution and compensation processes. However, our work has been restricted to the limit of low  $\text{MgO}$  (2 mol.%) concentration, and so the above effect is not expected to occur.

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