CONTROL OF THE Fe$^{2+}$ CONCENTRATION
IN IRON-DOPED LITHIUM NIOBATE*†

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The conversion of Fe$^{3+}$ to Fe$^{2+}$ in LiNbO$_3$ has been investigated and two techniques for accomplishing this without producing reduction of the host crystal are described. Annealing Fe-doped crystals in argon or argon-oxygen mixtures converts up to about 90% of the Fe to Fe$^{2+}$. Greater amounts are converted by annealing the crystals in oxygen or air while they are packed in powdered Li$_2$CO$_3$. These techniques are of use to optimize crystals for various holographic storage applications.

Key words: lithium niobate, hologram storage, divalent iron.

Introduction

Volume phase holography is emerging as an important technique for high density information storage. One of

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the most useful materials developed for this application is iron-doped lithium niobate.\(^1,2\) The storage of holograms in this material involves photoexcitation of electrons out of occupied traps and their subsequent recapture by empty traps. It has been established that the occupied traps are provided by Fe\(^{2+}\) ions and the empty traps by Fe\(^{3+}\) ions.\(^3,4,5,6\) Therefore, the concentrations of these ions play an important role in determining the quantitative parameters of hologram storage in the material, particularly the record sensitivity, erasure sensitivity, and maximum diffraction efficiency. In previous work \(^3,4,6\) it was demonstrated that these concentrations could be changed by oxidizing or reducing heat treatments. However, little information was provided on the production of controlled amounts of Fe\(^{2+}\). Some of the valence change methods employed led to reduction of the LiNbO\(_3\) host in addition to increasing the Fe\(^{2+}\) concentration. The purpose of the present paper is to describe techniques we have developed to produce a wide range of Fe\(^{2+}\) concentrations in LiNbO\(_3\) crystals without the introduction of extraneous host absorption. Since the holographic storage behavior of Fe-doped LiNbO\(_3\) appears to be insensitive to the presence of charge compensating ions or to changes in the stoichiometry of the crystals,\(^3,4\) this work was confined to crystals with the congruently melting composition, \(^7\) doped only with Fe.

Two classes of holographic storage applications have emerged for LiNbO\(_3\), each with its own requirements: (1) read-only storage and (2) read-write storage. Read-only storage, in which large numbers of holograms are stored and then "fixed" by the thermal fixing technique,\(^8\) requires a low erase sensitivity, while read-write storage requires a high erase sensitivity. Through careful choice of the overall Fe doping level of the LiNbO\(_3\) and the degree of reduction of Fe\(^{3+}\) to Fe\(^{2+}\), it has proven possible to optimize the properties of the material for either of these applications. Preparation of Fe-doped LiNbO\(_3\) for read-write applications is particularly difficult because it requires conversion of a very large fraction of the Fe ions into the divalent state.\(^5\) Two techniques for achieving this condition, annealing at high temperatures in argon and annealing in powdered Li\(_2\)CO\(_3\), are described here in detail. In addition, we describe the production of intermediate amounts of Fe\(^{2+}\) by annealing in argon-oxygen mixtures.