

Inorganic materials for optical data storage

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MS received 6 May 1981

Abstract. Recyclable holographic (optical) storage in inorganic materials is nowadays possible due to the advent of laser. Various performance parameters of the state-of-the-art of optical storage are discussed in detail with reference to the well-established case of ferroelectric lithium niobate (LiNbO_3). Various physicochemical techniques are employed in understanding the microscopic mechanisms responsible for optical storage in LiNbO_3 . A short summary of other inorganic materials capable of holographic storage is also presented.

Keywords. Ferroelectric LiNbO_3 ; optical storage; photorefractive effects; holography; laser.

1. Introduction

Optoelectronic devices have recently attracted considerable attention and there is every reason to believe that in the modern fields of science and technology such as optical communications, optical holography for information storage and display, etc., these devices will become very important in the next few years (Lines and Glass 1977). The invention of laser revealed in the early seventies a diversity of new methods for optical information storage. The revival of interest in photorefractive and photochromic materials, especially in inorganic oxidic materials, is due to our increased knowledge about the details of the impurity states in solids and of availability of extra pure materials (Faughnan *et al* 1971). In particular, a new class of ABO_3 type ferroelectric materials have been in the forefront as optical memory materials because their large electro-optic effects allow efficient read-out of the stored information.

There are three principal advantages of light in a storage system; (a) the use and transfer of light is very simple, no connections, as in the case of electrical systems and no vacuum, as in the case of electron beams. By means of acousto-or electrooptical procedures, the light can be either deflected or deviated very elegantly; (b) Very high packing densities may be obtained. Light may be focussed to a spot of diameter of the order of wavelength so

that the density of 10^8 bits/cm² can be obtained in a plane. The use of holographic methods and of the third dimension enhances the storage capacity to a theoretical limit of 10^{12} bits/cm³; and (c) the parallel access brings about extremely high data rates – 10^6 pages/sec with 10^5 bits/page can be read. To utilize optical methods for information storage with all the advantages, appropriate storage materials are absolutely necessary. The stringent requirements for these materials are

- (i) high optical and mechanical stability,
- (ii) simple to handle: no vacuum, no low temperatures, no wet chemical deposition, etc.,
- (iii) high sensitivity for recording at small recording energy,
- (iv) small recording time of the order of a few microseconds,
- (v) high optical resolution, especially in the case of holographic methods.

The transition metal ions doped ABO₃-type crystals, in particular, iron-doped lithium niobate, has proved very successful in optical information storage (Staebler and Phillips 1974; Alphonse *et al* 1975). The storage process in iron-doped lithium niobate single crystals has been generally attributed to a bulk photovoltaic effect and to the subsequent diffusion and drift of the photocarriers. The generation of photovoltaic, drift and diffusion currents by non-uniform light illumination causes an electronic space charge distribution which modulates the index of refraction *via* the electro-optic effect. By selectively doping the transition metal impurity ions in lithium niobate, the storage process can be enhanced by the orders of magnitude indicating the fundamental role of the impurities. In iron-doped lithium niobate, the impurities act as donor-acceptor traps *via* inter-valence exchange, such as $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$, to modulate, the index of refraction *via* the electro-optic effect (Keune *et al* 1975, 1976; Date *et al* 1976, 1981). However, the details of the mechanism are not clearly understood at the present time. In particular, the nature of charge carriers, transport processes, etc. have been the subject of extensive theoretical and experimental investigations in the last few years. The aim of the present paper is to summarize the work on memory storage and its origin done so far on the Fe:LiNbO₃ system using various experimental techniques. Although there are many suitable materials available in the literature, we will not give any details; however, a short discussion will be presented in the later part of the paper about other materials (Bordogna *et al* 1972).

2. Iron-doped ferroelectric lithium niobate (Fe : LiNbO₃)

The basic phenomenon involved in writing of phase holograms by the photo-refractive processes in materials such as lithium niobate is the photo-induced redistribution of electrons among the trapping centres. In the case of LiNbO₃, which can be grown as large crystals of high optical quality, Fe impurities are added to enhance the storage sensitivity. An overview is presented of the physical basis, experimental set-up and operating parameters for the information storage and read-out; structural, optical, ESR, Mossbauer and magnetic results are also presented for better understanding of the involved microscopic mechanisms.

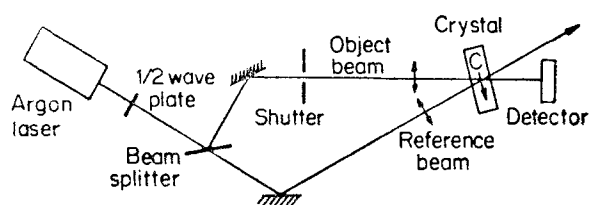


Figure 1. A schematic diagram in a hologram storage experiment. The polarisation vectors are in the plane of intersection as is the c -axis of the crystal.

2.1 Experimental set-up

A schematic diagram of the hologram storage apparatus is shown in figure 1. The polarisation vectors are in the plane of intersection as is the c -axis (optic axis) of the crystal. For storage, the crystal is exposed to both beams and for read-out or erasure, only to the reference beam. The storage holograms are fixed in the crystal by heating it in argon atmosphere at around 1000°C and then cooled rapidly to room temperature. To record a hologram, the crystal is exposed to two intersecting coherent light beams, which form an interference pattern. Photoexcitation of the trapped electrons creates a corresponding pattern of free electrons ($\text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+}$). These electrons can then migrate due to the drift in the uniform electric field present along c -axis and diffusion caused by the periodic gradients in the free carrier densities. In the successive steps of excitation, migration and retrapping, the electrons are rearranged to form a space-charge (high light intensity to low light intensity) field which modulates the refractive index of the material *via* the electro-optic effect. This gives a phase hologram storage.

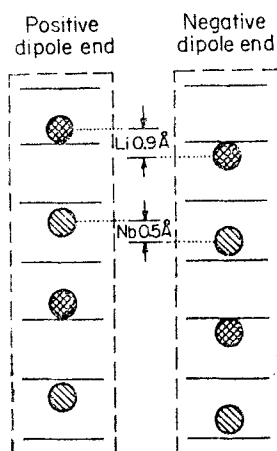


Figure 2. Li and Nb atoms along c -axis in LiNbO_3 .

2.2 X-ray structure data

The structure of LiNbO_3 is closely related to that of corundum ($\alpha\text{-Al}_2\text{O}_3$); it is obtained by replacing the two Al^{3+} with Li^{1+} and Nb^{5+} alternately, followed by some lattice distortion (Nassau 1967). In figure 2, the horizontal lines represent layers of oxygens, with the gap between the oxygen layers containing the sequence Li^{1+} , Nb^{5+} , vacancy or its inverse depending on the polarity of the c -axis. All three sites, the Li^{1+} , the Nb^{5+} and the neutral vacancy site have distorted octahedral oxygen environments (C_3) at room temperature. Accordingly, if an impurity atom is inserted in LiNbO_3 structure, it will not be possible to distinguish between these sites on the basis of experiments depending on the co-ordination number and site symmetry. In the case of iron-doped LiNbO_3 , ESR optical and ME data show a unique site occupancy of impurity iron ions, which will be discussed in the following sections.

2.3 ESR results

Herrington *et al* (1972) have carried out the electron spin resonance studies of iron impurities in LiNbO_3 at 9.4 and 35.4 GHz. Figure 3 shows the ESR spectra

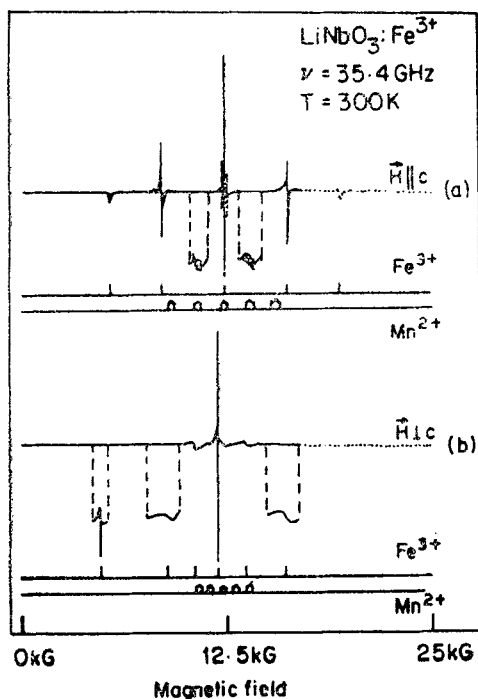


Figure 3. EPR spectra observed ($\nu = 35.4 \text{ GHz}$) for a $\text{LiNbO}_3:\text{Fe}$ single crystal at room temperature with (a) $H \parallel c$ and (b) $H \perp c$. The first derivative of absorption is shown versus magnetic field. Schematic diagrams are placed below each trace to ease the interpretation. The sections of each trace between the vertical dashed lines were recorded at 10 times the gain of the original trace. The dashed portions of each trace (17.5-25 kG) were not actually recorded due to magnet limitations. The line marked f in (b) is the $-1/2 \leftrightarrow 5/2$ transition.

observed at 35.4 GHz for a $\text{LiNbO}_3:\text{Fe}$ single crystal at room temperature with (a) $H\parallel C$ and (b) $H\perp C$. These spectra show that the impurity iron ions are in trivalent state and in sites of axial symmetry with the symmetry axis parallel to the crystallographic c -axis. The two substitutional sites in LiNbO_3 with this site symmetry are the Li^{1+} site the Nb^{5+} site. It is believed, therefore that the Fe^{3+} ions substitute for either Li^{1+} or Nb^{5+} ions in LiNbO_3 lattice and the charge compensation is remote.

2.4 Optical measurements

As indicated earlier, the amount of colouration for a given crystal depends on the fraction of the traps that are occupied (Fe^{2+}) which in turn depends upon the oxidation/reduction state of the crystal. Figure 4 shows a typical optical absorption spectra of occupied traps (Fe^{2+} ions) in a reduced LiNbO_3 single crystal (Stabler and Phillips 1974). A fully oxidized Fe -doped LiNbO_3 crystal contains only empty traps (Fe^{3+} ions, as seen also in ESR spectra) which do not contribute appreciably to colouration. Similar colouration is also observed in optical spectra when Fe -doped LiNbO_3 is packed in powdered Li_2CO_3 and annealed at temperatures between 450°C and 600°C . Figure 5 shows a set of optical spectra of Fe -doped LiNbO_3 annealed at various temperatures with Li_2CO_3 powder (Alphonse and Phillips 1976).

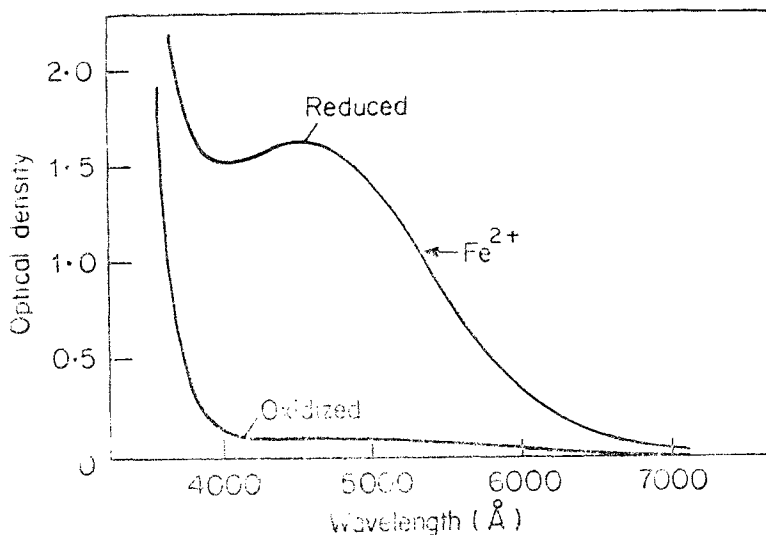


Figure 4. Optical absorption of occupied traps (Fe^{2+} ions) introduced by reduction heat treatments. A fully oxidized Fe -doped LiNbO_3 crystal contains only empty traps (Fe^{3+} ions) which do not contribute appreciably to the absorption. The rising absorption for wavelengths shorter than 4000 \AA is due to the electronic absorption edge of LiNbO_3 .

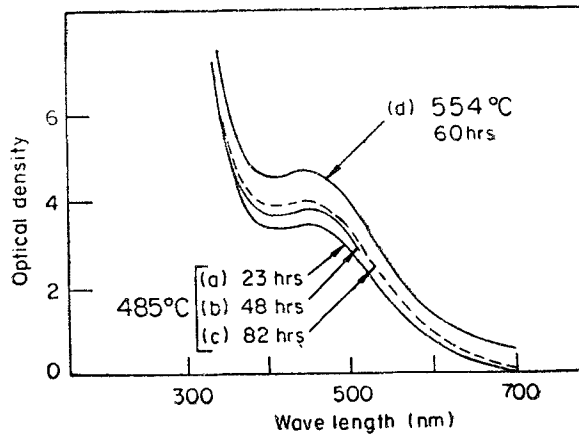


Figure 5. Optical absorption spectrum of $\text{LiNbO}_3:\text{Fe}$ single crystal annealed in Li_2CO_3 powder.

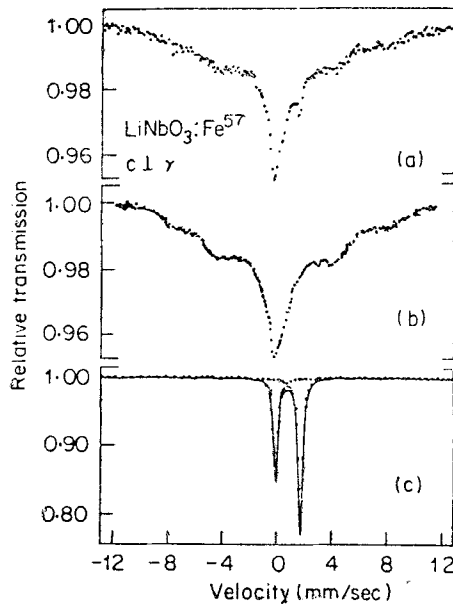


Figure 6. (a) Spectrum of a $\text{LiNbO}_3:\text{Fe}^{57}$ absorber at 295 K in original preparation state (estimated Fe concentration about 0.1 at. %), c axis perpendicular to γ direction; (b) same absorber as in (a) but after annealing in air at 800°C for 24 hr; (c) $\text{LiNbO}_3:\text{Fe}^{57}$ absorber at 295 K after annealing in Ar at 800°C for 24 hr (estimated Fe concentration about 0.2 at. %), c -axis perpendicular to γ direction.

2.5 Mössbauer measurements

Mössbauer effect (ME) spectra of iron doped LiNbO_3 have been recorded after various oxidation/reduction treatments at different temperatures between 4.2°

to 1000°C and in the presence of external magnetic fields ranging from 0-50 kOe (Date *et al* 1976, 1978, 1979, 1981). Figure 6 shows ME spectra of $\text{LiNbO}_3:\text{Fe}^{57}$ matched against a standard single-line source at room temperature after different oxidation/reduction treatments. The spectra show the oxidation of LiNbO_3 single crystal stabilizes Fe^{3+} state only in the lattice (figure 6b) while the reduction in argon atmosphere for a very long time (24 hr) stabilizes the Fe^{2+} state (figure 6c). The detailed hyperfine interaction analysis for the oxidized crystal shows in conformity with the optical and ESR data, the presence of Fe^{3+} ions in sites of axial symmetry. The reduction process in argon atmosphere has been studied in a step-wise process, as shown in figure 7. The single crystal orientation experiments and magnetic perturbation experiments on a polycrystalline absorber reduced in argon atmosphere show the presence of Fe^{2+} ions in sites of axial symmetry without any charge-compensating oxygen vacancy association (figures 8-9). The ME spectra of $\text{LiNbO}_3:\text{Fe}^{3+}$ single crystal

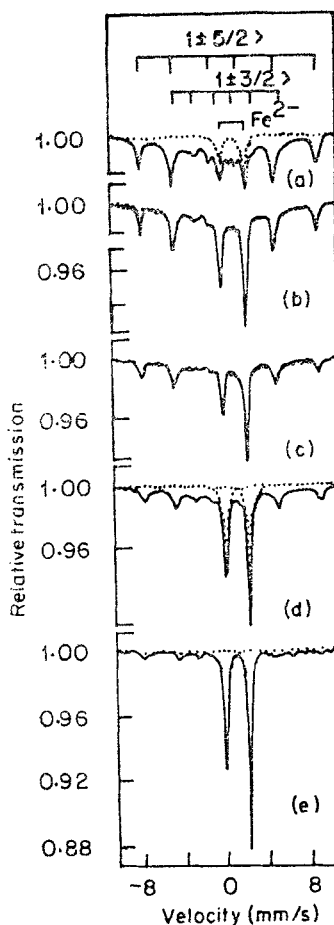


Figure 7. ——— Mossbauer spectra of a LiNbO_3 :—0.22 W % $\text{Fe}_2^{57}\text{O}_8$ absorber measured at 77 K after various annealing procedures at 1000°C: (a) as grown, (b) 760 torr argon atmosphere, 50h (c) 760 torr Ar, additional 50 h (d) 760 torr Ar, additional 10 hr (e) 0.2 torr Ar, additional 20 hr (c-axis always perpendicular to γ -ray).

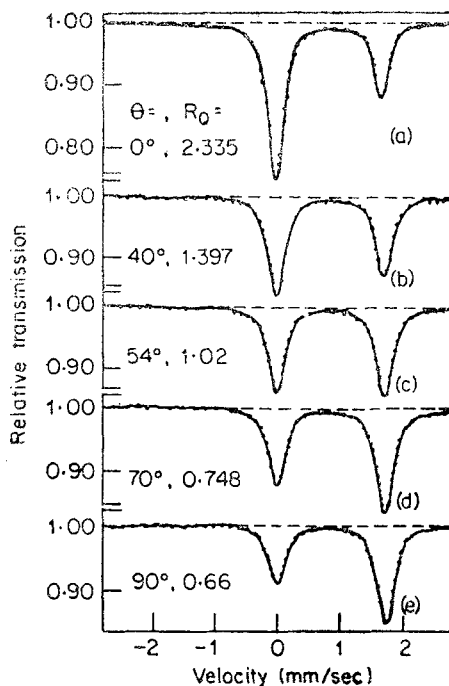


Figure 8. Mossbauer spectra of iron doped lithium niobate single crystal for different orientations with respect to gamma ray direction (a) zero degree (b) 40 degree (c) 54 degree (d) 70 degree (e) 90 degree.

reduced in the presence of Li_2CO_3 powder show also the formation of Fe^{2+} ions in the lattice (figure 10).

3. Microscopic models

Various microscopic models have been proposed to explain the storage process in Fe doped LiNbO_3 . Chen *et al* (1968) have proposed that the free carriers excited in the illuminated region are displaced along the polar c -axis of the crystal to the trapping sites. Johnston (1970) has attributed the photorefractive processes in LiNbO_3 to the presence of Nb^{5+} excess and stacking fault defects. Glass *et al* (1974) have proposed that the asymmetric charge transfer process and Frank-Condon shifts of the excited ions occur along c -axis of LiNbO_3 . An alternative approach to identify the trapping sites has been proposed by Dischler and Rauber (1975) which requires the splitting of the impurity energy levels due to the lowering of the symmetry, *i.e.* the formation of oxygen vacancy associated complex. Recently, Jonker and Lambeck (1978) have developed a model to explain charge transfer by assuming the pair formation of defects having dipole character and orientation of these dipoles parallel to the axis of polarisation, c -axis in LiNbO_3 .

All these models require a knowledge of the nature of trapping sites on a microscopic scale. In other words, it is necessary to know, in great detail, the various factors related to the electronic structure of the impurity ions such as

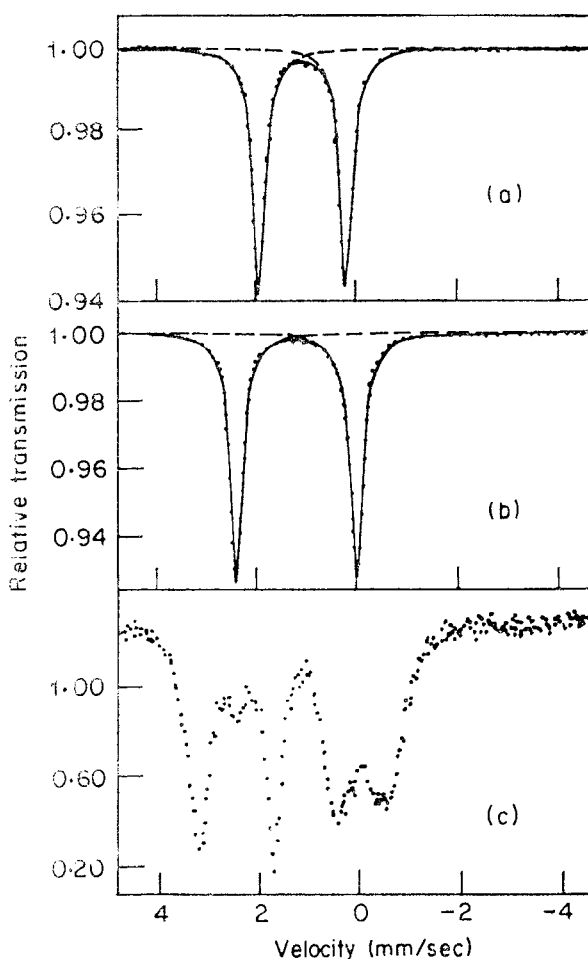


Figure 9. Mossbauer spectra of a polycrystalline absorber reduced in argon atmosphere at (a) 295 K, (b) 15 K, and (c) at 15 K and in the presence of an external magnetic field of 50 kOe.

valence state, the associated metal-ligand bond, the type of co-ordination of the surrounding polyhedron and also to the form of orbital ground state wavefunction, etc. As indicated in earlier sections, very interesting physicochemical studies have been carried out to identify these trapping centres and associated mechanisms responsible for photoexcitation from these centres. For example, ESR studies have identified a unique axial Fe^{3+} centres without any oxygen vacancy association. These ions play the role of empty traps and the occupied traps can be considered as the same ions in a reduced valence state i. e. $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$. The occupied traps introduce the characteristic optical absorption due to the photoexcitation of the trapped electrons into the conduction band. In a reduced crystal, the absorption band around 4800 Å has been identified as due to the Fe^{2+} centre in LiNbO_3 . It is also seen that the amount of colouration for a given crystal depends on the fraction of these traps that

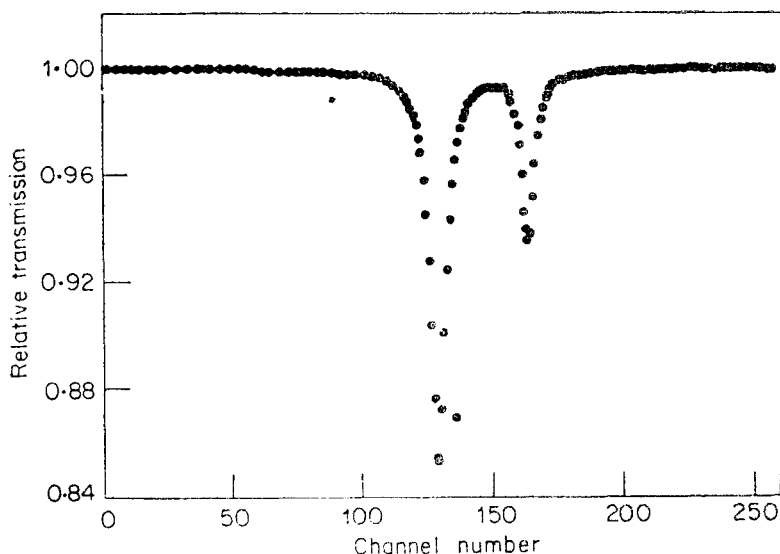
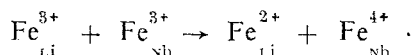


Figure 10. A quadrupole split spectrum after reduction with Li_2CO_3 powder.

are occupied which in turn depends upon oxidation/reduction of the crystal. Fe^{57} ME studies have proved most successful in the determination of valence exchange ($\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$) in lithium niobate in a direct way. These results limit the choice from the various models suggested so far in the literature. For example, the model of Dischler and Rauber (1975) requires the splitting of the impurity energy levels due to the lowering of the symmetry of oxygen octahedra, i.e. the formation of a $\text{Fe}^{2+}\text{-V(O)}$ pair, which is not observed either in ESR or in ME spectra. If $\text{Fe}^{2+}\text{-V(O)}$ pair is to be formed in sufficient concentration for the observation in ME spectra, single crystal and magnetic perturbation experiments must have shown clearly the deviation from axial symmetry (i.e. $\eta \neq 0$), which is not experimentally observed. Recently, Jonker and Lambeck (1978) proposed a model for LiNbO_3 based on a photo-activated charge transfer process



It requires equal occupation of Li and Nb sites by the impurity iron ions (Fe^{3+}). In ME spectra, there is no evidence of the formation of Fe^{4+} state in reduced crystal either in an argon atmosphere or in Li_2CO_3 powder, supported in an indirect way through optical studies. On the other hand, x-ray diffraction studies show considerable distortion of local crystal structure leading to a change in crystal lattice parameters and diffraction maximum broadening. It is clear from the above discussion that the intervalence exchange and Frank-Condon shifts of the impurity ions along the polar axis are most likely mechanisms responsible for storage process in LiNbO_3 . Surface and interface effects may also play an important role in the photorefractive processes in these materials (Date *et al* 1981).

3.1 Other materials (Bordogna *et al* 1972)

3.1a *Magneto-optic recording materials:* These materials utilize the Faraday or the Kerr effect for read-out of information. Writing is achieved by local heating with the help of light and simultaneous alignment of magnetization in an external magnetic field. MnBi films have been used for direct storage of digital information or for holographic storage of digital or pictorial information. The major drawbacks are the need to write in a very short time and low diffraction efficiency of MnBi holograms. Although two other materials, gadolinium iron garnet (GdIG) and europium oxide (EuO) have been studied, MnBi films appear to be best candidate for the magneto-optic holographic storage.

3.1b *Photochromic materials:* These materials have the ability to switch colours under the influence of optical irradiation. The colour is due to the transfer of an optically-excited electron from one type of colour centre to another, absorption properties of both centres changed accordingly. Irradiation at one wavelength produces a given change in colouration and the material returns to its original state when exposed to light of another wavelength. Examples of inorganic photochromic materials are silver halides, photochromic glasses, $\text{BaF}_2:\text{La}$, $\text{SrTiO}_3:\text{Fe/Mo}$, etc. The major advantage is that there is an inherent resolution limit, since the absorption takes place on an atomic or molecular scale. The disadvantages are image deterioration due to both thermal decay and optical bleaching during read-out, the fact that two wavelengths must be used for writing and erasing.

3.1c *Ferroelectric-photoconductor materials:* In this type of materials, a combination of a ferroelectrics and a photoconductor is used for information storage. With the help of external electric fields, the polarization is switched and these fields are controlled by a photoconductor. The appropriate materials used in the storage are $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Gd}_2(\text{MoO}_4)_3$, lead zirconate-titanate ceramics and CdS, CdSe. These materials are not yet severely tested for commercial applications.

There are other materials being tested for future technological applications: this discussion does not tell the complete story. Many factors such as difficulty in fabrication, projected cost and reproducibility are not discussed. It is hoped that the sustained research efforts will develop new exciting materials for holographic storage of information.

4. Conclusions

It has been demonstrated that holographic (optical) storage in inorganic materials such as Fe-doped LiNbO_3 is nowadays feasible. The storage processes are understood in terms of intervalence exchange between the impurity ions and its associated electronic defect structure.

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