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APPLICATION OF THERMAL ANALYSIS TO STUDY THE CRYSTAL GROWTH, DEFECT STRUCTURE AND THERMAL EXPANSION OF $LiNbO_3$

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ABSTRACT

Single crystals of $LiNbO_3$ are used in a variety of electro-optical devices. For switches, the lightguides are generally fabricated by diffusing TiO_2 into prescribed paths on single crystal wafers. A valuable property of $LiNbO_3$ is its high ferroelectric transition, $T_c \approx 1140$ °C, which allows the processing to be achieved without depoling the crystal.

Highly perfect homogeneous crystals are necessary for such devices. Since $LiNbO_3$ melts incongruently, the crystals must be grown at exactly the proper non-stoichiometric melting point. The T_c is highly dependent upon Li concentration and hence DTA can be used as an analytical tool to determine the exact congruent composition, i.e., 48.45 M% Li_2O, and as a means of subsequent quality control. In addition T_c is a function of the general defect structure of the material and is used to study the effects of additives such as TiO_2 upon the cation vacancy content and phase equilibria.

For precise alignment of optical fibers with the lightguides it is necessary to know the thermal expansion values for these highly anisotropic crystals. Such data are obtained through careful dilatometric measurements. These measurements also reveal a poorly defined transition in congruent $LiNbO_3$ crystals at about 120 °C.

INTRODUCTION

As the use of fiber optic cables for transmission in telecommunications systems grows, the quest for integrated optical devices increases. Currently, one of the most promising optical switching devices involves the use of single crystal $LiNbO_3$.[1] Switching is achieved by applying an appropriate voltage to the crystalline region between adjacent channel waveguides. These waveguides are formed within the poled single crystal $LiNbO_3$ substrate by depositing Ti metal in the desired pattern on the surface, oxidizing it to TiO_2 and then diffusing those lines of TiO_2 into the $LiNbO_3$ to form waveguides that have a semicircular cross section with a slightly higher refractive index. The advantages of $LiNbO_3$ beyond its electrooptical properties are the ability to grow large single crystals of the material and the high Curie temperature (T_c) of the resulting crystal. This latter point allows the higher temperature processing steps, e.g., in diffusion of TiO_2, to occur at temperatures which generally will not depole the crystal substrate.

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Thermoanalytical methods are particularly valuable for studying several of the critical properties and processes associated with the formation of these optical switches. The following is a list of such aspects.

1. Analysis of the extent of lithium deficiency in these $Li_{1-x}NbO_{3-0.5x}$ materials.
2. Determination of the precise congruent composition required to grow homogeneous crystals from the melt.
3. Understanding the effects of additives such as TiO_2 upon the phase equilibria and T_c of these crystals.
4. Measurements of thermal expansion to facilitate compatibility of packaging materials to preserve the critical alignment of the components.

In subsequent sections of this review we will address these items sequentially and show how thermal analysis has contributed crucial insights along with essential data and understanding necessary to produce viable optical switches.

ANALYSIS OF COMPOSITION

The phase diagram for the Li_2O-Nb_2O_5 system is presented in Fig. 1.[2]. The incongruent melting of the material referred to is evident. The ferroelectric transition within the single phase $Li_{1-x}NbO_{3-0.5}$ field is indicated by the dashed line. It can be seen that there is a pronounced dependence of this transition upon the Li content or value of x. A convenient and accurate method of determining this transition temperature would thus provide a useful analytical tool. Differential thermal analysis (DTA) is commonly used to detect phase transitions and has been demonstrated to be adequately sensitive in this specific system in spite of the higher order nature of this ferroelectric transition.[3,4] DTA curves are shown in Fig. 2 for crushed single crystal material having both the stoichiometric composition and a sample having near the congruent composition. The weak nature of this higher order transition is evident as the small step in the congruent curve near 1140 ℃ arising from the ΔC_p at the transition temperature (T_c). The extrapolated onset is used herein to establish the exact value of T_c. The stoichiometric crystal is made by diffusing Li into the

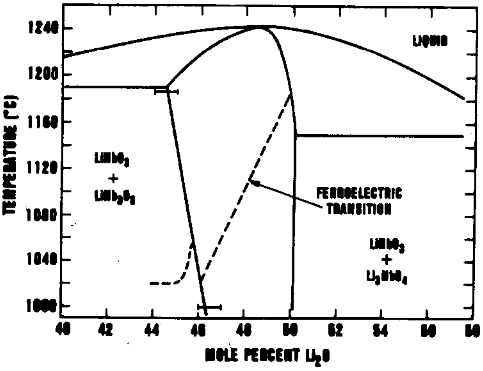

Fig. 1. Phase Diagram for a portion of the system Li_2O-Nb_2O_5 (Ref. 2).

congruent crystal. From Fig. 1 it can be seen that T_c of the stoichiometric composition can not be determined under equilibrium conditions without some melting. The latter process has a large change of enthalpy which masks the much smaller thermal effect at T_c. This early melting and large endotherm are obvious in Fig. 2 for the stoichiometric composition. The T_c of the stoichiometric material, however, can be

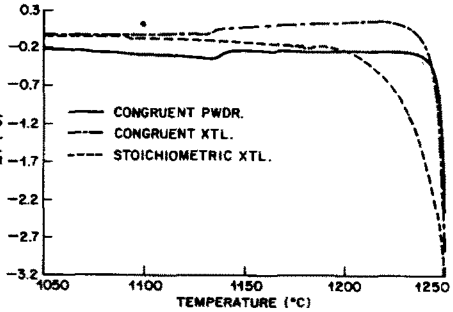

Fig. 2. DTA curves for stoichiometric and congruent $LiNbO_3$ (20℃ $\cdot min^{-1}$ in N_2); 48.6 mol% Li_2O + 51.4 mol% Nb_2O_5 mixed and reacted at 1100℃ for 300h: (------) source powder 92.84 mg; (--- - ---) crushed as grown crystal, 117.26 mg: (- - - -) crushed stoichiometric crystal, 86.42 mg. [4].

measured by the change in slope occurring. in the thermal expansion curves. Dynamic thermodilatometry is used to derive the thermal expansion curves for single crystals shown in Fig. 3.[4] The changes in slope at T_c are much more obvious for the curves parallel to the c-axis of the crystal.

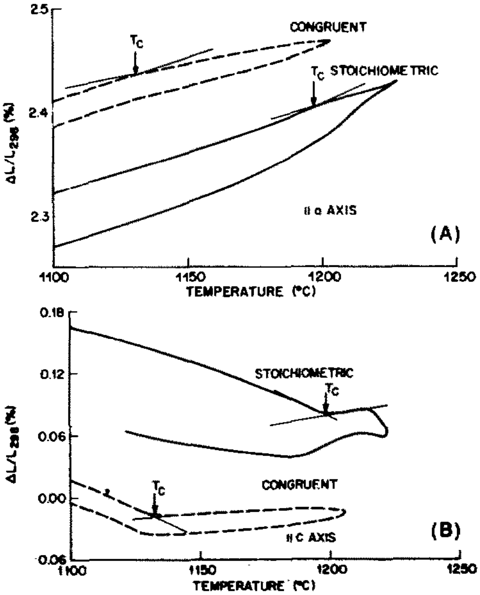

Fig. 3. Thermal expansion along (A) a axis and (B) c axis for stoichiometric and congruent $LiNbO_3$ above 1100℃ (4℃$\cdot mm^{-1}$). [4].

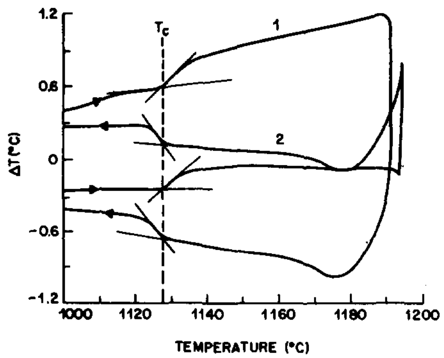

Fig. 4. DTA curves for two samples of crushed congruent crystal of $LiNbO_3$ (20 ℃·min^{-1} in N_2); (1) 164.00 mg and (2) 148.74 mg. [4].

There is very little temperature hysteresis in the ferroelectric transition, even at 20 ℃ min.$^{-1}$ This is evident from the heating and cooling curves shown in Fig. 4 for two separate samples of a crushed single crystal. The excellent reproducibility is also obvious. The accuracy of the transition temperature is assured by using the nearby melting point of Au, at 1064.4 ℃, for calibration. Using a carefully prepared series of varying Li_2O to Nb_2O_5 contents it was possible to accurately establish the dependence of T_c upon composition.[3,5] Several sets of results are presented in Fig. 5. The two sets of DTA derived measurements[3,5] are in excellent agreement at high and intermediate concentrations of Li but depart significantly at lower concentrations. The lines are least squares fits. The larger data set is fit by a second order equation:

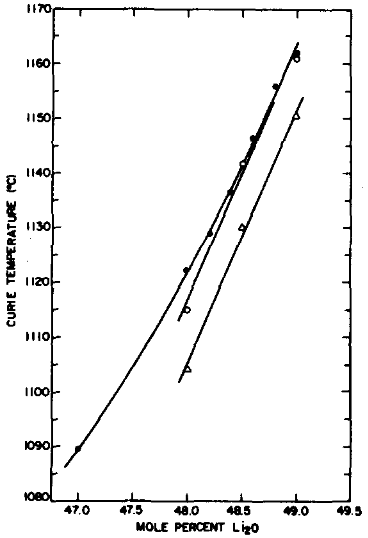

Fig. 5. Curie temperature vs. mol% Li_2O in $LiNbO_3$: (●) current work, (○) Ref. 3, (Δ) Ref. 6. [5].

$$T_c = 9095.2 - 360.05C + 4.228\,C^2 \qquad (1)$$

where C is the Li_2O content in mole %.

A much more cumbersome but versatile approach to establishing the Li_2O content has been pioneered by Holman.[7] This method involves surrounding the unknown sample by the two phase mixture adjoining the nonstoichiometric phase field, i.e., $LiNbO_3$+Li_3NbO_4 (see Fig. 1), and following the weight change of the sample by isothermal thermogravimetry, the two phase mixture establishes the precise Li vapor pressure associated with the phase boundary and at suitable temperatures the kinetics of vapor transport allow for the transfer of Li_2O to the sample until it equilibrates at that vapor pressure and temperature. If the position of the phase boundary is well known, then the initial degree of nonstoichiometry can be determined from the weight change. Either phase boundary could be used, if its position is well defined, but the direction of weight transfer reverses. A typical experimental representation is shown in Fig. 6.[7]

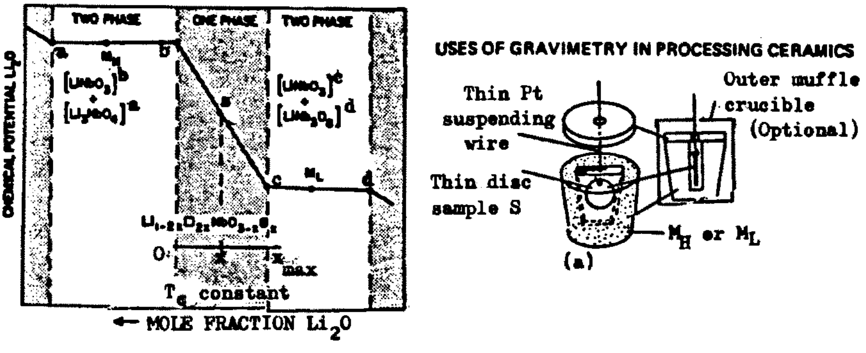

Fig. 6. Isothermal composition dependence of lithium oxide chemical potential in the Li_2O-Nb_2O_5 system. [7].

DETERMINATION OF THE CONGRUENT COMPOSITION FOR CRYSTAL GROWTH

From the analytical method described in the previous section and summarized by eq. 1 and Fig. 5, it is possible to precisely establish the congruent composition required for homogeneous crystal growth. The T_c of samples of the initial melt (essentially the samples used for Fig. 5), and final melt (after crystal growth) along with samples from the first and last grown portions of the crystal were measured by DTA. Assuming that diffusion in the solid is negligible and mixing in the liquid phase is perfect, it is possible to define a distribution coefficient of Li_2O. These values are plotted in Fig. 7 as a function of mole % Li_2O in the melt. An effective distribution coefficient of unity describes the congruent composition which appears to be at 48.45 mole % Li_2O. This is somewhat lower than the previously accepted value of 48.6 mole % Li_2O.[6]

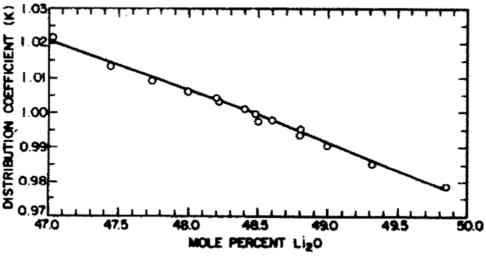

Fig. 7. Distribution coefficient vs mol% Li_2O in melt. [5].

When a crystal is grown from the congruent composition the Li content of both the melt and crystal should remain unchanged during the entire process. In Fig. 8 are shown the DTA curves for the initial and final melts as well as for the top and bottom portion of the resulting crystal. It can be seen the T_c is virtually identical for these samples based upon growth from a melt having 48.45 mole % Li_2O.

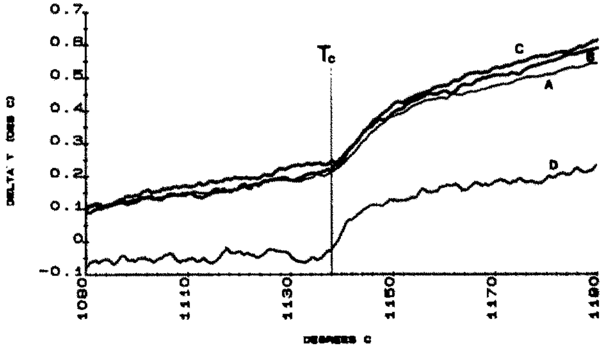

Fig. 8. DTA heating curves for (A) initial melt, (B) final melt, (C) top crystal, and (D) bottom crystal for growth from melt with initial 48.45 mol% Li_2O composition. [5].

The convenient and relatively rapid nature of the DTA technique for measuring T_c and hence for determining the Li content in materials has established it as the method of choice for quality control. We presently utilize DTA to assay the incoming pre-mixed cullet material used for crystal growth and then make modifications as necessary. Portions from the top and bottom of each crystal grown are also measured to establish the homogeneity along the vertical or growth axis of the crystal.

Recently, optical measurements indicated that there was a thin skin on these crystals which was of slightly different composition. A study using both techniques confirmed the presence of a Li_2O deficient thin skin on these crystals.[8] The DTA evidence is presented in Fig. 9 which clearly indicates the lower T_c of the material taken from the outer 2mm of the crystal. Fortunately, this inhomogeneous portion of the crystal is ground off in the normal process for preparing the polished wafers used as substrates.

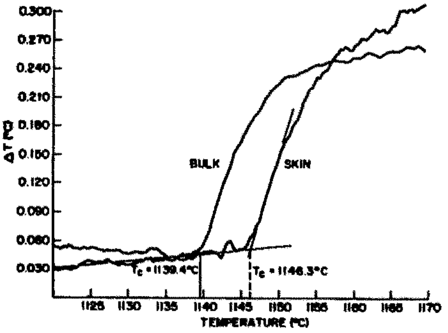

Fig. 9. DTA Curves of Samples From the $LiNbO_3$ Single Crystal, 20 ℃ min^{-1} in 60 ml min^{-1} O_2. [8]. Skin 157.46 mg - Bulk 152.72 mg.

EFFECTS OF TiO_2 ADDITIONS ON T_c AND DEFECT STRUCTURE

Abrahams and Marsh[9] have developed a model for the cation vacancy structure of $Li_{1-x}NbO_{3-0.5x}$ based upon their detailed x-ray diffraction study. Using this model as a basis Gallagher and O'Bryan[10] have expanded upon it to consider the addition of TiO_2 and other oxides to form solid solutions with both the congruent and stoichiometric compositions of $LiNbO_3$. There is not room in this brief review to derive the relationships needed, however, the final result for the defect concentration can be expressed by eq. 2, which is based upon the formula $Li_yNb_{1-y}Ti_xO_{2.5-2y+2z}$.

$$CV=2-4y+z \qquad (2)$$

where CV is the fraction of cation vacancies on the B site of the perovskite structure.

The interesting outcome of this work is summarized in Fig. 10. It is apparent that the cation vacancy content determines T_c regardless of how these vacancies are created, e.g., lithium deficiency, TiO_2 addition, etc. The line in Fig. 10 describes the linear relation between T_c and CV while the extra coordinates on the right side indicate how T_c and CV correspond to lithium content in the absence of other additions and the scales on top show how the additions of TiO_2 correlate for either the congruent or the stoichiometric lithium contents.

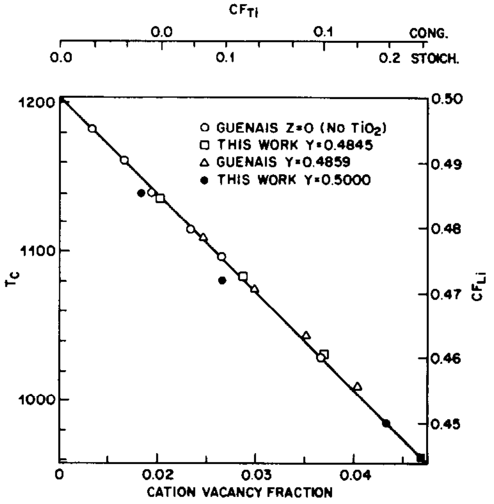

Fig. 10. Plot of T_c, cation fraction of Ti added to either stoichiometric or congruent $LiNbO_3$ and cation fraction of Li as a function of cation vacancy fraction for $LiNbO_3$ (T_c from Ref. 3). [10].

The observation that T_c does not drop below 963 ℃ for the addition of large amounts of TiO_2 is indicative of the solubility limit of TiO_2 in a particular $LiNbO_3$ sample. The solubility limit is determined by the value of CV. Therefore $LiNbO_3$ which already has a significant content of vacancies due to lithium deficiency will be able to dissolve less TiO_2. It is interesting to note that additions of MgO to $LiNbO_3$ will have the effect of annihilating cation vacancies, thereby raising both T_c and the amount of TiO_2 which can be dissolved.[11]

This depression of T_c, because of the cation vacancy formation resulting from additions of TiO$_2$ has several profound effects upon the potential device performance of optical switches. As the vacancy content surpasses the critical value, a second phase will precipitate in the waveguide and induce scattering losses. Similarly, even if the solid solubility is not exceeded, the value of T_c may be reduced below the processing temperature for Ti in diffusion and thereby depole the crystal. This too will induce scattering within the waveguide leading to insertion losses associated with the device. Clearly the insights provided by Fig. 10 are critical to the preparation of satisfactory optical switches from LiNbO$_3$.

THERMAL EXPANSION OF LiNbO$_3$

Alignment and its preservation is critical to virtually all optical components in a telecommunications system. Consequently, detailed knowledge of the thermal expansion for each component is essential. Earlier in Fig. 3 it was demonstrated how thermodilatometry could be used to detect the ferroelectric phase transition. In Fig. 11 the thermal expansion is shown over the range from 100-1000℃ for both a stoichiometric and congruent single crystal of LiNbO$_3$. There is considerable anisotropy evident from the data. Expansion parallel to the c-axis actually goes through a maximum at a temperature which varies with Li content. The differences between the expansion of the stoichiometric and congruent crystals along each axis cancel each other and there is the no difference in the unit cell volumes as a function of temperature.

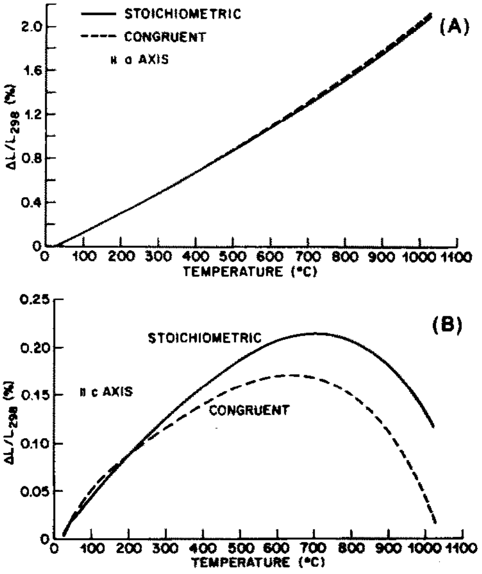

Fig. 11. Thermal expansion along (A) a axis and (B) c axis for stoichiometric and congruent LiNbO$_3$ (4 ℃· min^{-1}). [4].

For determining accurate expansion values near room temperature it is necessary to begin the heating program well below room temperature in order to have a steady heating rate through the region of interest. While performing such a study [12] a transition was noted in the congruent crystal around 100℃, see Fig. 12, which was not evident for the stoichiometric crystal. This step in the thermal expansion coefficient indicates that it is a higher order transition. It is much more prominent in the expansion along the c-axis than along the a-axis. Confirmation of the transition was subsequently obtained by other techniques as well.[12]

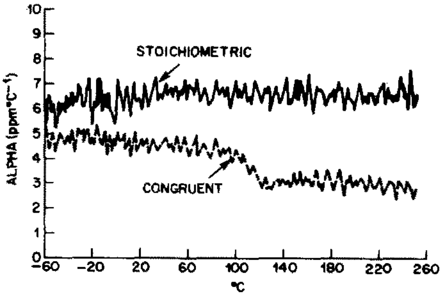

Fig. 12. Thermal expansion coefficient of $LiNbO_3$ single crystal along the c-axis. [12].

CONCLUDING REMARKS

Clearly thermal analysis has proved most useful in studies of the phase equilibria, crystal growth and properties of $LiNbO_3$. It has provided a technique to analyze the concentration of cation vacancies and, therefore indirectly, the lithium deficiency of the material or the concentration of various additives, e.g. TiO_2, or MgO. MgO. The extent of solubility can also be determined from the point at which the T_c remains constant upon further addition of these materials. Besides these indirect benefits, the value of T_c sets a lower limit on the processing temperature that can be used and still preserve a single domain crystal.

This analytical method has been used to establish the congruent composition essential for the growth of homogeneous single crystals. The method is so fast and convenient that it is most suitable as a tool for quality control. Finally, it has been shown that thermal analysis can be used to obtain such important thermal properties as the thermal expansion and in doing so has pointed out a transition around 100 ℃. It is the purpose of meetings such as this International Congress on Thermal Analysis to facilitate, stimulate and encourage, the exchange or interaction of ideas between those of us active in different spheres of materials science but sharing the common thread of utilizing thermoanalytical techniques. The example of $LiNbO_3$ is but one of many that can be made for the extensive use of thermal analysis for the characterization of ceramics and other inorganic materials.

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