

Investigation of Nonstoichiometry and Ferroelectric Properties in the Ternary System $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$ at 1250°C under Atmospheric Pressure

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X-ray crystallographic studies conducted at atmospheric pressure have allowed determination of the limits of solid solutions with LiTaO_3 structure in the ternary system $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$. Stoichiometry analysis has shown that the prevailing type of nonstoichiometry of these phases is simultaneous cationic and anionic deficits. Dielectric measurements carried out on the ceramic samples showed a decrease in the ferroelectric Curie temperature as the composition deviates from that of pure LiTaO_3 . © 1987 Academic Press, Inc.

1. Introduction

LiNbO_3 and LiTaO_3 are essential materials in the manufacture of various devices of importance in different fields of modern technology: optical wave guides, electrooptics, pyroelectric arrays, SAW IF filters, SHG, etc. (1-16). Most of the physical properties exploited in these practical applications are very sensitive to the quality and quantity of impurities and to small deviations from the stoichiometry, LiMO_3 ($M = \text{Nb}, \text{Ta}$) (1-3, 17-29). For example, the well-known phenomenon labeled "optical damage" or "photorefractive effect" has been found to be closely related to certain types of impurities, particularly iron cations (1, 8, 17, 26, 29-32). This optical degradation, desirable for materials to be used for holography and phase conjugation,

must be prevented when these materials are needed for nonlinear applications in the blue-green spectral region (30). The damage resistance is substantially increased if a percentage (threshold of 4.5%) of MgO is added to the congruent melt during the growth of LiNbO_3 single crystals (17, 34-36). Although intensive research has been conducted in order to understand the effect of impurities and stoichiometry deviation on the physical properties of LiMO_3 ($M = \text{Nb}, \text{Ta}$), only scattered results relating to nonstoichiometry are available in the literature, except in the case of tetravalent cations M'^{4+} ($M' = \text{Ti}, \text{Zr}, \text{Sn}$) for which a nearly complete study of all types of nonstoichiometry has been published recently (9-14, 36). We have now completed the former study and can present a complete view of nonstoichiometry and ferroelectric properties in the ternary system $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$.

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2. Sample Preparation

Standard solid solution techniques were used for the synthesis of powder samples. Materials of the desired compositions were prepared from the appropriate mixtures of starting materials, Li_2CO_3 , Ta_2O_5 , and WO_3 , of analytical grade. Several heat treatments of 12-hr duration interspersed by grinding were necessary to obtain a pure single phase. Firing temperatures varied between 600 and 1250°C. All chemical reactions were conducted in air, under atmospheric pressure. Verification of weight losses (before and after heat treatment) and X-ray analysis were used for checking of purity and structural characterization of the freshly synthesized materials. The solid solutions investigated in the ternary diagram are represented by lines A, B, C, D, E, F, G, H, I, and J in Fig. 1.

Ceramic samples for dielectric measurements were prepared by sintering pressed pellets at 1250°C in air under atmospheric pressure. The disks obtained have diameter and thickness of about 13 and 1 mm, respectively. Dielectric constants were determined from the capacitance of the con-

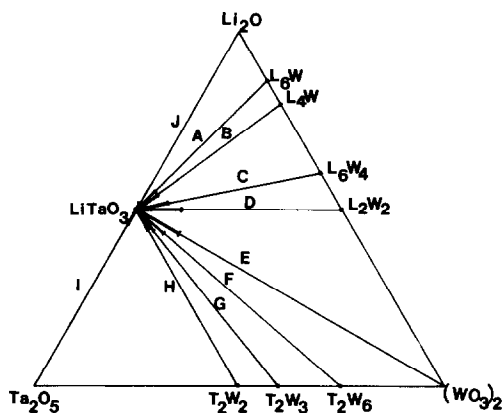


FIG. 1. Domain extension (—) of the solid solutions investigated (line A → J) in the ternary system $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$. $\text{L}_6\text{W} = \text{Li}_6\text{WO}_6$; $\text{L}_4\text{W} = \text{Li}_4\text{WO}_5$; $\text{L}_6\text{W}_4 = \text{Li}_6\text{W}_4\text{O}_{15}$; $\text{L}_2\text{W}_2 = \text{Li}_2\text{W}_2\text{O}_7$; $\text{T}_2\text{W}_2 = \text{Ta}_2\text{W}_2\text{O}_{11}$; $\text{T}_2\text{W}_3 = \text{Ta}_2\text{W}_3\text{O}_{14}$; $\text{T}_2\text{W}_6 = \text{Ta}_2\text{W}_6\text{O}_{23}$.

denser prepared by deposition of silver or gold paste on both flat faces of the pellets.

3. Analysis of the Variation of Nonstoichiometry in the Ternary System $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$

The crystal structure of LiTaO_3 has been determined by Abrahams *et al.* (38). It can be described as an ordered corundum structure where 2 Al^{3+} are replaced by 1 Li^+ and 1 Ta^{5+} . The hexagonal unit cell contains 18 LiTaO_3 units. The space groups of the ferroelectric and paraelectric phases are, respectively, $R3c$ and $R\bar{3}c$.

Since the stoichiometric LiTaO_3 lattice contains one cationic vacancy for each O_3 set and can accommodate no excess anions, only the six following possibilities of stoichiometry change can be considered for this structural type, assuming that the cations can only fill the octahedral sites of the hexagonal close packed oxygen sublattice:

Oxygen sublattice undergoes no change:

- (1) Same stoichiometry as in LiTaO_3
- (2) Cationic deficit
- (3) Cationic excess

Oxygen sublattice with vacancies:

- (4) Anionic deficit alone
- (5) Simultaneous anionic and cationic excess

(6) Coupled anionic and cationic deficit
Figure 2 shows the regions of the ternary diagram where these types of nonstoichiometry are located (37).

Any composition derived from LiTaO_3 along the lines $\text{Li}_2\text{O}-(\text{WO}_3)_2$, $\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$, or $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5$ must have the chemical formula

$$\square_{1+\alpha} A_{\beta}^{+p} B_{\gamma}^{+q} \text{O}_{3-\delta} \Delta_{\delta}, \quad (1)$$

where \square and Δ stand for cationic and anionic vacancies, respectively.

Along the line $\text{Li}_2\text{O}-(\text{WO}_3)_2$ we have $A = \text{Li}$, $B = \text{W}$, $p = 1$, and $q = 6$ while along the line $\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$ we have $A = \text{Ta}$, $B = \text{W}$, $p = 5$, and $q = 6$. According to the crystal

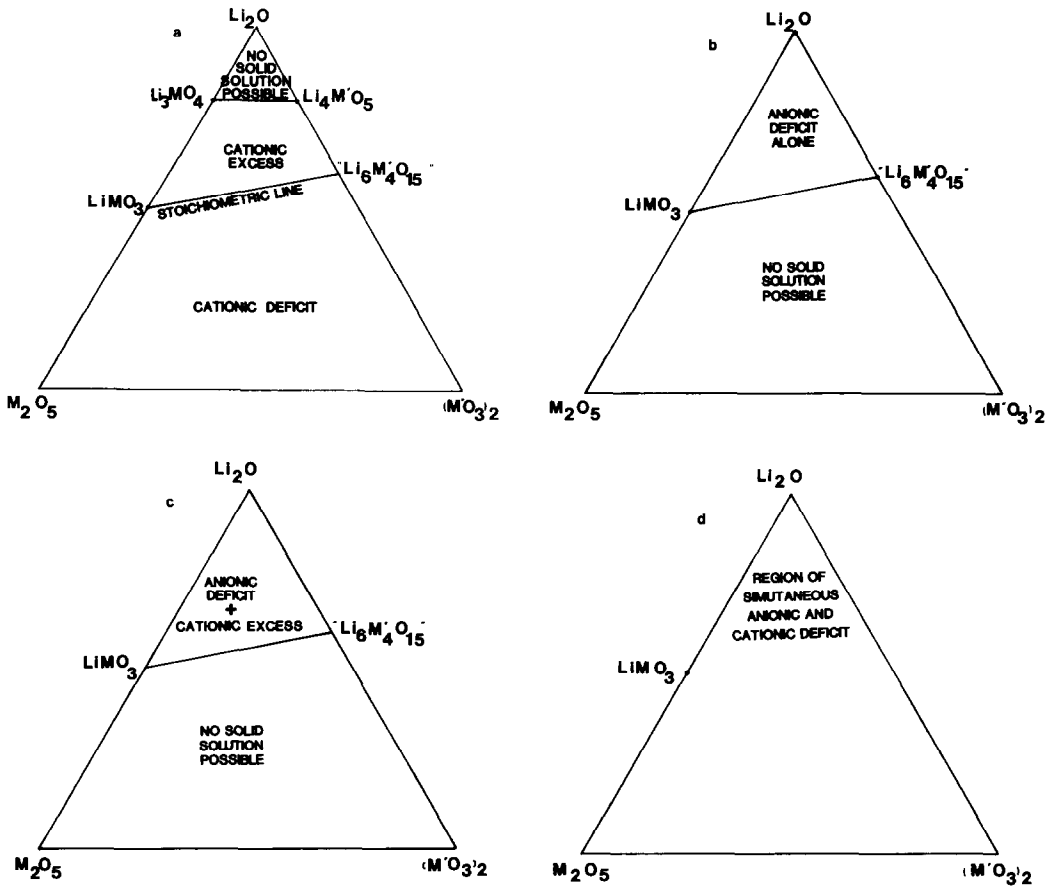


FIG. 2. Summary of all types of nonstoichiometry related to LiTaO_3 structure and their localization in the ternary diagram $\text{Li}_2\text{O}-\text{M}_2\text{O}_5-(\text{M}'\text{O}_3)_2$ ($M = \text{Nb, Ta}$; $M' = \text{hexavalent cation}$). (a) Oxygen sublattice undergoes no changes; (b) region of anionic deficit alone; (c) region of simultaneous anionic deficit and cationic excess; (d) region of coupled anionic and cationic deficits.

structure and charge neutrality of the lattice, the system of equations

$$\alpha + \beta + \gamma = 2 \quad (2)$$

$$p\beta + q\gamma + 2\delta = 6 \quad (3)$$

$$\gamma = n\beta \quad (4)$$

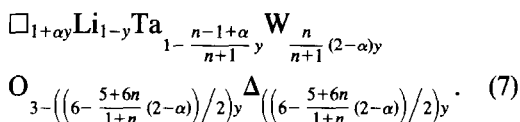
can be derived from Eq. (1), which could then be written as follows:

$$\square_{1+\alpha} A_{2-\frac{\alpha}{n+1}}^{+p} B_{\frac{\alpha}{n+1}}^{+q} \text{O}_{3-\left(6-\frac{p+qn}{1+n}(2-\alpha)\right)/2} \Delta_{\left(6-\frac{p+qn}{1+n}(2-\alpha)\right)/2} \quad (5)$$

The general formula of every solid solution starting at LiTaO_3 ($x = 0$) and ending on any point of the line $\text{Li}_2\text{O}-(\text{WO}_3)_2$ ($x = 1$) can be expressed by

$$\square_{1+\alpha} \text{Li}_{1-\frac{n-1+\alpha}{n+1}x} \text{Ta}_{1-x} \text{W}_{\frac{n}{n+1}(2-\alpha)x} \text{O}_{3-\left(6-\frac{1+6n}{1+n}(2-\alpha)\right)/2} \Delta_{\left(6-\frac{1+6n}{1+n}(2-\alpha)\right)/2} \quad (6)$$

In the case of the solid solutions between LiTaO_3 ($y = 0$) and any point along the line $\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$ ($y = 1$), the chemical formula is given by



The general formulas Eqs. (6) and (7) can describe all cases of nonstoichiometry summarized in Fig. 2, and allowed for any composition having the LiTaO_3 structure, in the ternary system. The exact crystal chemical formula of every solid solution studied can be determined according to Eqs. (6) and (7) and from the fit of the calculated and

measured values of the density for each value of x and y . Table 1 gives, for example, the crystal chemical formulas determined from the density measurements plotted in Fig. 3. The type of nonstoichiometry obtained for these lines corresponds to the coupling of cationic and anionic deficits, possibility 6. In all cases we note the existence of a measurable anionic deficit, contrary to the results recently obtained in the similar systems, $\text{Li}_2\text{O}-\text{M}_2\text{O}_5-(\text{M}'\text{O}_2)_2$ ($M = \text{Nb, Ta}$; $M' = \text{Ti, Zr, Sn}$), where no evidence for anionic deficit has been detected

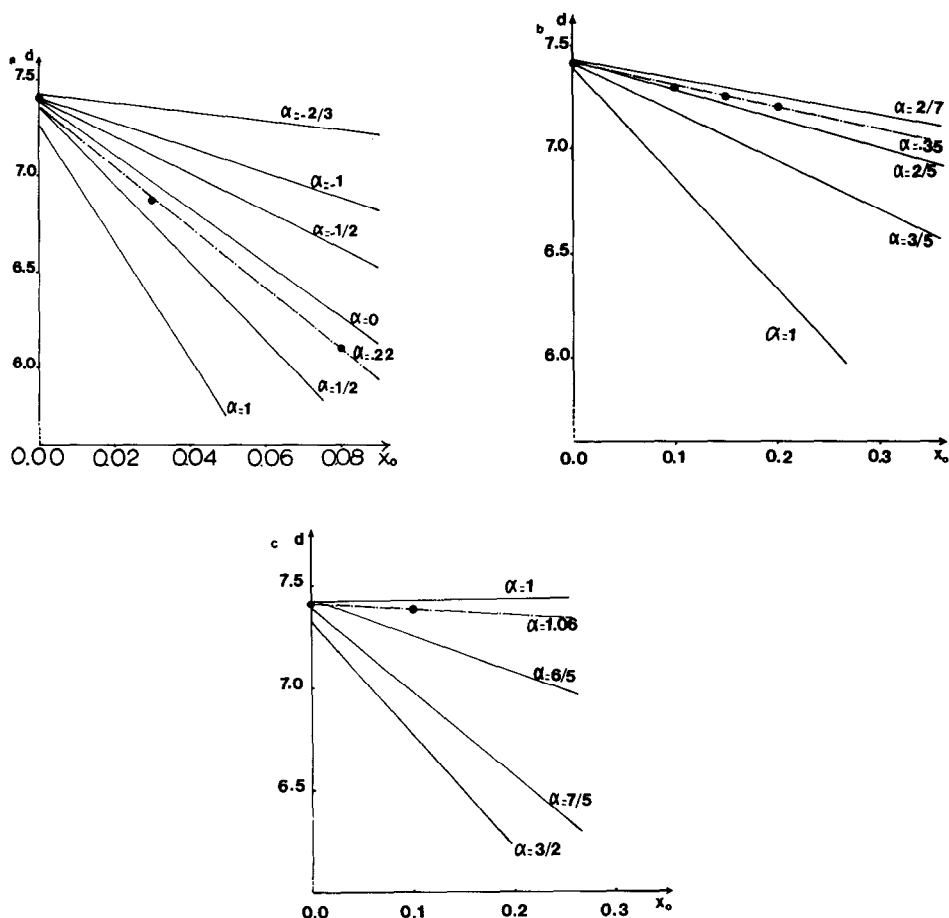


FIG. 3. Typical density (d) variation curves obtained along the lines A (a), line D (b), and line E (c). Theoretical values of density are calculated from Eq. (6), where n is equal to $\frac{1}{2}$, 1, and ∞ for lines A, D, and E, respectively. The values of α are indicated on each corresponding plot. ●, Experimental values; —, theoretical values.

TABLE I
CHEMICAL FORMULAS OF LINES A, D, AND E AS
DETERMINED FROM EQ. (6) AND FIGS. 3-5,
SHOWING EVIDENCE FOR SIMULTANEOUS CATIONIC
AND IONIC DEFICITS

Line	Chemical formula of the corresponding solid solution
A	$\square_{1+0.22x}\text{Li}_{(7+3.68x)/7}\text{Ta}_{1-x}\text{W}_{1.78x/7}\text{O}_{3-10.32x/7}\Delta_{10.32x/7}$
D	$\square_{1+0.35x}\text{Li}_{1-0.175x}\text{Ta}_{1-x}\text{W}_{0.825x}\text{O}_{3-0.1125x}\Delta_{0.1125x}$
E	$\square_{1+1.06x}\text{Li}_{1-x}\text{Ta}_{1-x}\text{W}_{0.94x}\text{O}_{3-0.18x}\Delta_{0.18x}$

within the limits of our experimental procedures (4-7, 39). The existence of an anionic deficit in the present work is supported by the fact that many of the synthesized samples (with high values of x and y in Eqs. (6) and (7)) have faint to deep green or yellow colors, while similar samples with Ti, Zr, or Sn have the white color of LiTaO_3 and no perceptible anionic deficit. This is not surprising since the solid state syntheses of all these compounds were conducted under atmospheric pressure ($P_{\text{O}_2} \approx \frac{1}{5}$ atm). These experimental conditions, under which tungsten compounds seemed to be more sensitive, are probably providing a reducing atmosphere; and it is normal to expect coloration of the samples resulting from either oxygen vacancies or valence change of

some cations or both. It is also to be noted that the green coloration has previously been observed in lithium-deficient LiNbO_3 by Lerner *et al.* and Nassau *et al.*, who suggested the possibility of attributing this coloration to traces of chromium (25, 40). We are currently conducting an ESR study to clarify the origin of this color in samples of the ternary system, $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$. This technique has proved to be very useful for the study of the impurity behavior in LiNbO_3 and LiTaO_3 ; extensive research has been published in this field by Halliburton and co-workers (41-45).

4. Crystal Chemical Analysis

The limits of the solid solutions investigated were determined by the appearance of impurity diffraction lines in the X-ray patterns of the samples. Trigonal space group $R3c$ (hexagonal indexing) has been used for the systems. One does not expect a big change in the unit cell parameters, both because solid solutions extend over relatively narrow regions and because all cations incorporated in the LiTaO_3 network have similar ionic radii: $r(\text{Li}^+) = 0.68 \text{ \AA}$, $r(\text{Ta}^{5+}) = 0.68 \text{ \AA}$, and $r(\text{W}^{6+}) = 0.62 \text{ \AA}$ (46). This assumption is confirmed by the experimental results plotted in Fig. 4. Along some

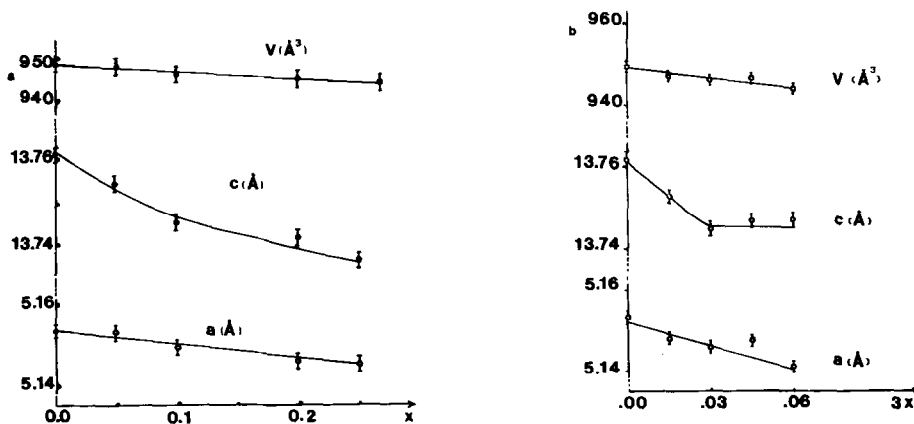
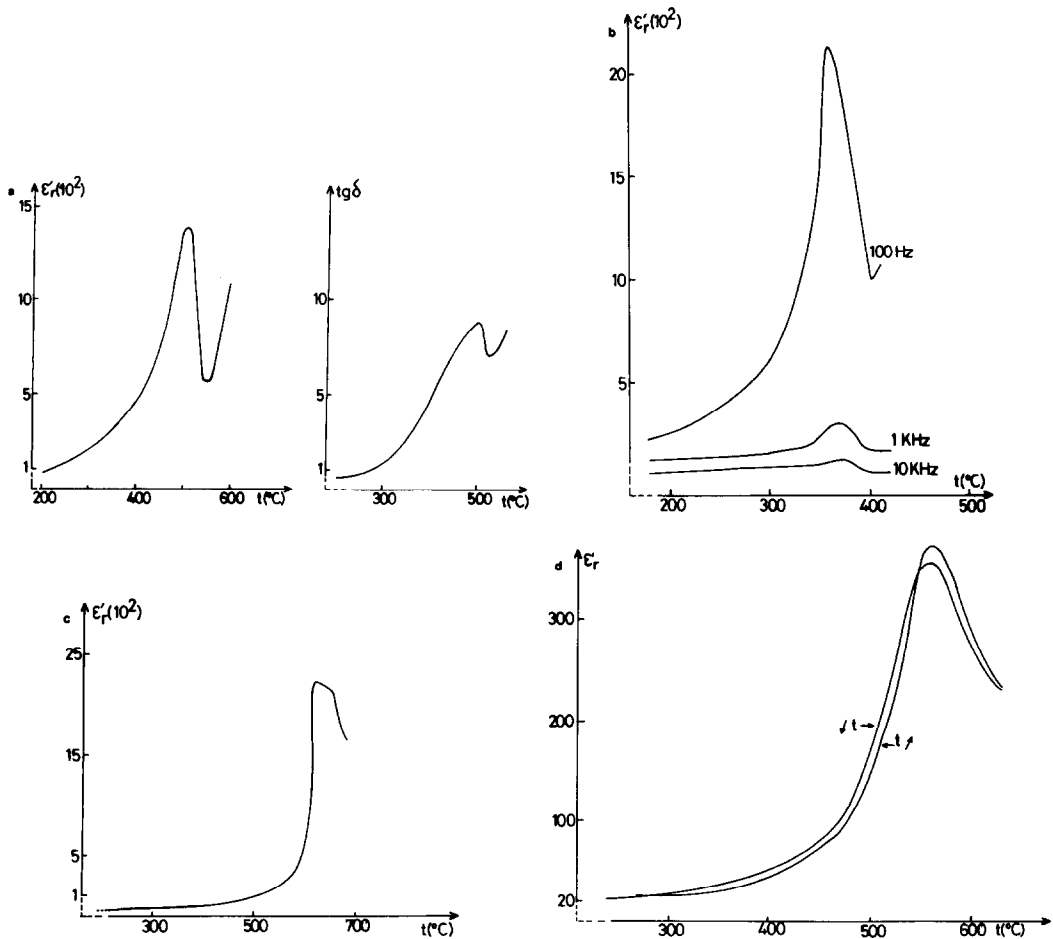


FIG. 4. Typical variation of lattice parameters versus composition along lines E (a) $\text{Li}_{1-x}\text{Ta}_{1-x}\text{W}_x\text{O}_3$ and B (b) $\text{Li}_{1+7x}\text{Ta}_{1-5x}\text{W}_{3x}\text{O}_3$.

TABLE II
 SOME CHEMICAL AND PHYSICAL DATA CONCERNING LINES A TO J

Line	Chemical formula	Number of cations (NC)	$\gamma = \text{NC} - 2$	Upper limit of x	Max. value of W cation molar fraction	T_C (°C)
A	$\text{Li}_{1+4x}\text{Ta}_{1-2x}\text{W}_x\text{O}_3$	$2 + 3x$	$3x$	0.08	0.0357	380
B	$\text{Li}_{1+7x}\text{Ta}_{1-5x}\text{W}_{3x}\text{O}_3$	$2 + 5x$	$5x$	0.02	0.0286	370
C	$\text{Li}_{1+x}\text{Ta}_{1-5x}\text{W}_4\text{O}_3$	2	0	0.0375	0.075	540
D	$\text{Li}_{1-x/7}\text{Ta}_{1-x}\text{W}_{6x/7}\text{O}_3$	$2 - \frac{2}{7}x$	$-\frac{2}{7}x$	0.25	0.1111	435
E	$\text{Li}_{1-x}\text{Ta}_{1-x}\text{W}_x\text{O}_3$	$2 - x$	$-x$	0.25	0.1429	620
F	$\text{Li}_{1-x}\text{Ta}_{1-(17/23)x}\text{W}_{(18/23)x}\text{O}_3$	$2 - \frac{22}{23}x$	$-\frac{22}{23}x$	0.23	0.10112	607
G	$\text{Li}_{1-x}\text{Ta}_{1-(47/14)x}\text{W}_{(9/14)x}\text{O}_3$	$2 - \frac{13}{14}x$	$-\frac{13}{14}x$	0.20	0.0709	538
I	$\text{Li}_{1-x}\text{Ta}_{1+x/5}\text{O}_3$	$2 - \frac{4}{5}x$	$-\frac{4}{5}x$	0.12	0.00	485
J	$\text{Li}_{1+x}\text{Ta}_{2-x/5}\text{O}_3$	$2 + \frac{4}{5}x$	$+\frac{4}{5}x$	0.07	0.00	640


 FIG. 5. Thermal variation of ϵ_r for various lines: A (a) composition $\text{Li}_{1.16}\text{Ta}_{0.92}\text{W}_{0.04}\text{O}_3$ B (b) composition $\text{Li}_{1.14}\text{Ta}_{0.90}\text{W}_{0.06}\text{O}_3$ C (c) composition $\text{Li}_{1.015}\text{Ta}_{0.925}\text{W}_{0.06}\text{O}_3$ G (d) composition $\text{Li}_{0.901}\text{Ta}_{0.943}\text{W}_{0.064}\text{O}_3$.

lines investigated, for example, line A, there is practically no detectable change in the unit cell parameters over the existing domain of the solid solution. Some chemical and physical data for lines A to J are presented in Table II. The solid solubility of WO_3 in LiTaO_3 was investigated by Blasse *et al.*, who reported the existence of a continuous solid solution with LiTaO_3 structure up to 30% WO_3 (47). This limit is very close to the one obtained in this work (Table II). The formulas given in Table II are those written with the oxygen stoichiometry fixed at O_3 and are not intended to mean that the oxygen sublattice has no deficiencies (see Table I); such an expression simplifies comparison of these results with those of our previous study of the systems $\text{Li}_2\text{O}-\text{M}_2\text{O}_5-(\text{M}'\text{O}_2)_2$ (4-7, 39). We note also that the most extended solid solution of the ternary diagram, $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-\text{WO}_3$, is along the line E, for which the ratio Li/Ta remains constant (Table II).

5. Dielectric Study

Thermal variation of the dielectric constant has been used to determine the ferroelectric Curie temperature (T_C) at the peak of the $\epsilon_r'(T)$ curve. Dielectric measurements were performed on ceramic samples with a Hewlett-Packard (4262A) capacitance bridge. Heating and cooling rates of 0.25 to $1^\circ\text{C}/\text{mn}$ were used. Figure 5 shows some results obtained for solid solutions A, B, C, and G. The temperature (T_C) at the peak of each $\epsilon_r'(T)$ curve allows plotting the variation of the ferroelectric Curie temperature vs composition as shown in Fig. 6. This figure shows that the drop of T_C is much sharper along the lines A, B, C, and D than along E, F, and G. It is probably related to the ratio $r = (\text{Li}/\text{Ta})$ since the A, B, C, and D lines correspond to $r > 1$ while E, F, and G correspond to $r \leq 1$.

It is also clear from Table II and Fig. 6 that line E holds the solid solution (contain-

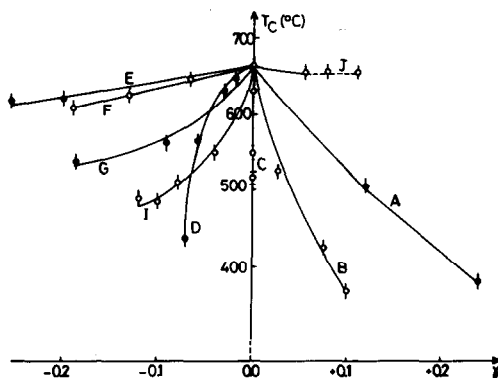


FIG. 6. Variation of the ferroelectric Curie temperature vs γ in the diagram $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$.

ing W cations) which corresponds to the lowest decrease in T_C vs composition, suggesting that it is probably along this line that LiTaO_3 lattice is least perturbed by the coupled substitution related to this solid solution. The upper limit ($\text{Li}_{0.75}\text{Ta}_{0.75}\text{W}_{0.25}\text{O}_3$) of the solid solution E is the composition of the diagram which contains the maximum percentage of W incorporated in the LiTaO_3 network (Table II).

Summary and Conclusions

Our crystal-chemical study of the ternary diagram $\text{Li}_2\text{O}-\text{Ta}_2\text{O}_5-(\text{WO}_3)_2$ shows the existence of continuous solid solutions along all the lines investigated. Unlike the results known for similar systems with TiO_2 , ZrO_2 , or SnO_2 , simultaneous cationic and anionic deficits have been observed in the LiTaO_3 network when W is introduced. Dielectric measurements performed on ceramic samples have shown that T_C decreases in all cases, as the stoichiometry deviates from LiTaO_3 .

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