

Ordering Phenomena in the LiSbO_3 Type Structure: The New Mixed Tellurates $\text{Li}_2\text{TiTeO}_6$ and $\text{Li}_2\text{SnTeO}_6$

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$\text{Li}_2\text{TiTeO}_6$ and $\text{Li}_2\text{SnTeO}_6$, synthesized at 700°C , are orthorhombic, with $a = 5.072 \text{ \AA}$ (5.192), $b = 4.903 \text{ \AA}$ (4.927), and $c = 8.402 \text{ \AA}$ (8.513) for Ti (Sn). The structure of the Ti compound, space group $Pbn2_1$, has been deduced from X-ray powder diffraction intensities: it derives from the LiSbO_3 structure by an additional Ti–Te ordering. This type of ordering is likely to occur also in $\text{Li}_2\text{SnTeO}_6$. Although not detectable by X-ray diffraction, it is supported by the sharpness of the bands in the vibrational spectrum. A comparison of ordering phenomena in $\text{Li}_2\text{TiTeO}_6$ – LiSbO_3 type—and $\text{Li}_2\text{ZrTeO}_6$ –corundum-like structure—is proposed. © 1989 Academic Press, Inc.

Introduction

Ordering phenomena of the cation distribution in octahedral sites seem to be a common property for mixed oxides of tellurium (VI). As an example, a highly ordered structure belonging to the corundum family was recently described for the compounds $\text{Li}_2\text{Zr(Hf)TeO}_6$ (1), which can be derived from the LiInbO_3 type structure (2) by the double substitution:



The occurrence of a $M^{\text{IV}}/\text{Te}^{\text{VI}}$ order in oxides with a LiSbO_3 type structure (3) is considered here. As a matter of fact, the synthesis of complex tellurates $\text{Li}_i\text{M}^{\text{IV}}\text{M}^{\text{III}}\text{Te}^{\text{VI}}\text{O}_6$ ($M^{\text{II}} = \text{Mg, Ni, Co, Zn}; M^{\text{III}} = \text{Fe, Cr, In}$) (4) points to a likely ordering phe-

nomenon in such a structure. Therefore, we checked the existence of a $M^{\text{IV}}/\text{Te}^{\text{VI}}$ order ($M^{\text{IV}} = \text{Ti, Sn}$) in ABO_3 oxides closely related to the LiSbO_3 type.

The present results deal with the preparation, crystal chemistry, and vibrational characteristics of new mixed tellurates with the formulas $\text{Li}_2\text{TiTeO}_6$ and $\text{Li}_2\text{SnTeO}_6$. An ordering phenomenon originating in the double substitution $2 \text{Sb}^{\text{V}} \rightarrow \text{Ti}^{\text{IV}} + \text{Te}^{\text{VI}}$ is described for the LiSbO_3 type structure of $\text{Li}_2\text{TiTeO}_6$ and compared to that observed in the corundum-like structure of $\text{Li}_2\text{Zr(Hf)TeO}_6$.

Experimental

The synthesis of $\text{Li}_2\text{TiTeO}_6$ was performed from stoichiometric mixtures of

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Li₂CO₃, TiO₂, and TeO₂ heated in platinum crucibles, in air. The initial temperature must not exceed 600°C in order to ensure a full oxidation of Te^{IV} into Te^{VI}. Then, annealing at 700°C during 2 days, with intermediate regrindings, leads to completion of the solid state reaction.

This procedure does not give pure Li₂SnTeO₆, since a small quantity of uncombined SnO₂ (easily detected by X-ray diffraction) is still present after 1 week at 720°C. Pure Li₂SnTeO₆ may be obtained by a two-step procedure: Li₂SnO₃ is first prepared by solid state reaction between Li₂CO₃ and SnO₂ (2 days at 1000°C); it is then mixed with a small excess (5 to 10 mol%) of TeO₂, and the mixture is progressively heated up to 600°C, and then annealed for 2 days at 700°C.

Radiocrystallographic analysis was made from a Gunitier Nonius camera; powder patterns were recorded with a Philips powder goniometer, both using the CuK α radiation.

IR and Raman spectra were obtained with conventional techniques and equipment.

Results

Using the experimental procedure described above, two new mixed tellurates Li₂TiTeO₆ and Li₂SnTeO₆ were obtained.

The thermal stability of these phases is moderate: after 1 day at 800°C, they are transformed into other phases, whose nature has not been investigated so far. In the case of the Ti compound, the actual results may be summarized as follows:

(i) No free TiO₂ (either rutile, anatase, or brookite) may be detected by X-ray diffraction. The transformation scheme is thus very different from that previously evidenced for Li₂Zr(HF)TeO₆ (1).

(ii) Only broad bands are observed in the IR spectrum of the decomposition prod-

uct(s), possibly suggesting some kind of disorder.

(iii) The transformation is reversible: annealing at 700°C for 1 day restores the initial Li₂TiTeO₆ phase.

Additional work is needed to solve this problem.

Powder patterns of these compounds are closely related to that of LiSbO₃. Therefore, they were indexed with an orthorhombic cell. Table I brings together the values of *a*, *b*, and *c* parameters obtained after a least-square refinement and the cell volume for Li₂Ti(Sn)TeO₆ and, for comparison, those observed for LiSbO₃ (3). These results confirm the geometrical relationship between the cells of these mixed tellurates and LiSbO₃. Moreover, the observed variations agree well with the predictions which can be drawn up from the mean ionic radii of cations. The lowest value of the cell volume for Li₂TiTeO₆ and the highest one for Li₂SnTeO₆ point to a significant difference between the mean size of the pairs (Ti^{IV}-Te^V) and (Sn^{IV}-Te^V) which are, respectively, smaller and larger than that of Sb^V.

Structural Determination of Li₂TiTeO₆

Comparing the indexing of the diffractogram of Li₂TiTeO₆ with that of LiSbO₃: space group $D_{2h}^6 Pnmn$, leads to the following conclusions:

(i) the reflection conditions for (*hkl*): $h + l = 2n$ and for (*0kl*): $k + l = 2n$ are observed;

(ii) the condition for (*hkl*): $h = 2n$ is no longer observed for Li₂TiTeO₆, owing, for instance, to the existence of (110) reflection with a significant intensity.

Given these conditions, and in agreement with the assumption made by one of us (P.T.) for the mixed tellurates LiM^{IV}M^{III}TeO₆ (4), we considered the space group $C_{2h}^{10} Pmn2$ to be the most probable. As a matter of fact, in that case the only reflec-

TABLE I
CRYSTALLOGRAPHIC DATA FOR THE ORTHORHOMBIC
CELLS OF $\text{Li}_2\text{Ti}(\text{Sn})\text{TeO}_6$ AND LiSbO_3 (3)

Compounds	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
$\text{Li}_2\text{TiTeO}_6$	5.072(1)	4.903(1)	8.402(2)	208.9
$\text{Li}_2\text{SnTeO}_6$	5.192(2)	4.927(2)	8.513(5)	217.7
LiSbO_3	5.183	4.893	8.491	215.3

Note. Parameters correspond to the choice of the standard space group for LiSbO_3 : $D_{2h}^6 Pnma$.

tion conditions are $(0kl)$: $k + l = 2n$ and $(h0l)$: $h + l = 2n$; moreover, as it is a subgroup of $D_{2h}^6 Pnma$, a structural model close to the LiSbO_3 type is likely to exist for $\text{Li}_2\text{TiTeO}_6$.

Structure calculations were undertaken from the integrated intensities of 39 reflections, i.e., 71 (hkl) . Starting from the model described for the structure of LiSbO_3 (3), Te and Ti occupy the positions 2(a): $00z$ and 2(b): $0yz$, respectively; in the same way there are two sets of Li atoms located in 2(a) and 2(b). All the oxygen anions are found in three sets of general positions 4(c): x, y, z . The initial value of the confidence

factor $R_1 = \sum |I_0 - I_c| / \sum I_0$ is close to 0.12: it ensures the validity of the LiSbO_3 structure as a model for $\text{Li}_2\text{TiTeO}_6$. Several least-squares refinements cycles were made (5), considering successively the distribution of Ti and Te over 2(a) and 2(b) sites, their atomic coordinates, that of oxygen, and, as a final step, that of Li; thus, the R_1 value falls to 0.038.

In Table II, we report the set of atomic parameters corresponding to the best value of R_1 and for comparison those determined for LiSbO_3 (3). It must be stated, first, that despite a much larger number of variable coordinates, 13 instead of 6, the values obtained here for $\text{Li}_2\text{TiTeO}_6$ are not significantly different from those of LiSbO_3 . Therefore, the main characteristic of the structure is found in the existence of an order in the distribution of Ti and Te over the Sb sites. Although the mathematical result does not point to complete ordering (94% is observed), it can be considered that a 1/1 order (only a 1% increase of R_1) is the most likely to occur between Ti and Te.

Table III brings a list of calculated and observed intensities and Table IV compares

TABLE II
ATOMIC PARAMETERS OF $\text{Li}_2\text{TiTeO}_6$: SG $Pmn2$ and LiSbO_3 (3): SG $Pnma$

Atoms	Positions	x	y	z	$R(\text{\AA})^2$	
(1) Li(1)	(1) 2(a)	(1) 0.0	(2) 0.0	(1) 0.0	(2) 0.723(7)	(1) 1 fixed
Li(2) Te	2(b) 2(a)	0.0 0.0	0.5 0.0	0.5 0.0	0.790(6) 0.1057(7)	1 fixed 1.0(1)
Ti	Sb	2(b) 4(c)	0.0 0.0	0.5 0.0	0.4026(7) 0.257(3)	0.0971 2.0(8)
O(1)	O(1)	4(c)	0.166(2)	0.194	0.250	1.3(8)
O(2)	O(2)	4(c)	0.669(2)	0.207(1)	0.078(4)	1.3(8)
O(3)	O(2)	4(c)	8(e)	0.657	0.209	0.081
				0.829(4)	0.793(2)	1.1(7)

Note. (1) $\text{Li}_2\text{TiTeO}_6$. (2) LiSbO_3 . (3) In order to facilitate the comparison with $\text{Li}_2\text{TiTeO}_6$, a shift of the origin, $-a/4$, is made for LiSbO_3 . (4) $R_1 = 0.038$ for $\text{Li}_2\text{TiTeO}_6$ is obtained with the distribution: 94% Te 6% Ti site 2(a), 6% Te 94% Ti site 2(b).

TABLE III
OBSERVED AND CALCULATED INTENSITIES FOR THE
X-RAY PATTERN OF $\text{Li}_2\text{TlTeO}_6$, $R_1 = 0.038$

$h k l$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	$h k l$	$I_{\text{obs.}}$	$I_{\text{calc.}}$
101	78.0	77.4	033	1.5	1.7
011	172.0	172.3	006	5.0	4.4
002			230		
110	16.0	16.1	321	5.0	5.3
112	101.0	101.4	133		
200	13.0	12.4	231		
103	26.0	26.0	224	28.0	28.2
020			215		
013	7.0	8.8	125	2.0	1.7
210	7.0	8.5	116	3.0	4.1
120	0.5	0.0	314	6.0	5.2
113	15.0	15.1	400		
211	40.0	40.4	134	7.0	6.9
202			323		
121	17.0	18.7	233	0.5	1.6
022	7.0	4.9	410		
004	7.0	6.7	206	5.0	5.0
114	12.0	10.1	040		
220			225		
213	31.0	31.7	026		
123			411	8.0	6.1
221	41.0	41.0	402		
301	4.0	4.4	141		
222	12.0	12.4	412	3.0	3.8
204			042		
031			330		
310			035		
105	29.0	28.4	107	6.0	6.5
024			017		
015			332		
130	1.0	1.5	420	8.0	9.0
312	20.0	17.6	413		
225			226		
132	17.0	16.6	143	7.0	8.3
303	15.0	14.0	241		

the main interatomic distances in $\text{Li}_2\text{TiTeO}_6$ and in LiSbO_3 . The following features must be emphasized:

— TeO_6 and TiO_6 octahedra, despite a low site symmetry, C_2 , are rather regular. The mean M -O distance is nearly the same in the two cases, 1.96 Å: it is slightly smaller than the mean Sb-O distance in LiSbO_3 , 2.03 Å. Moreover, as would be

predicted for a d^{10} cation as Te^{VI} , the regularity of the TeO_6 octahedra is greater.

—As a significant difference from LiSbO_3 , the LiO_6 octahedra seem to be significantly distorted. This is probably due to the existence of different neighboring octahedra (Ti and Te) around the LiO_6 octahedra.

Order Phenomena in $\text{Li}_2\text{SnTeO}_6$

We did not make any attempt to solve the structure of $\text{Li}_2\text{SnTeO}_6$, as the isotypism with LiSbO_3 does not create a problem. Nevertheless, it cannot be stated unambiguously that a Sn/Te order occurs. If one considers that the existence of a (110) reflection is a sensitive means of checking this order, it should be noted that this reflection is not found in the powder pattern of $\text{Li}_2\text{SnTeO}_6$. However, this is not inconsistent with a Sn/Te order. As Sn^{IV} and Te^{VI} are isoelectronic, their atomic scattering factors are almost identical. So the (110) reflection, which from the analysis of its structure factor can be considered as a "difference" reflection like in spinels (6), fully vanishes when Sn^{IV} and Te^{VI} simulta-

TABLE IV
MAIN INTERATOMIC DISTANCES (Å) IN $\text{Li}_2\text{TlTeO}_6$
AND LiSbO_3 (3)

Distances	$\text{Li}_2\text{TlTeO}_6$	LiSbO_3	Distances
Te-O(1)	($\times 2$) 1.97	($\times 2$) 2.00	Sb-O
Te-O(2)	($\times 2$) 1.98	($\times 2$) 2.04	
Te-O(3)	($\times 2$) 1.94	($\times 2$) 2.05	
Ti-O(1)	($\times 2$) 1.91		
Ti-O(2)	($\times 2$) 1.99		
Ti-O(3)	($\times 2$) 1.98		
Li(1)-O(1)	($\times 2$) 2.10	($\times 2$) 2.01	Li-O
Li(1)-O(2)	($\times 2$) 2.07	($\times 2$) 2.07	
Li(1)-O(3)	($\times 2$) 2.24	($\times 2$) 2.07	
Li(2)-O(1)	($\times 2$) 2.12		
Li(2)-O(2)	($\times 2$) 2.22		
Li(2)-O(3)	($\times 2$) 2.09		
$\Delta = 0.03$ - 0.06 Å			

neously occur. A neutron diffraction study will be undertaken in order to give good evidence of the Sn/Te order. Although, it cannot be deduced from the absence of the (110) reflection that there is no Sn/Te order, the analysis of the vibrational spectra provides evidence for the existence of ordering.

Vibrational Spectra

The IR and Raman spectra of both compounds are rather complex, with an interrupted succession of bands between 800 and 100 cm^{-1} . Moreover, the spectra of the Ti and Sn compounds are sufficiently different to prevent any band to band correlation between the spectra, and the ${}^6\text{Li}$ - ${}^7\text{Li}$ isotopic shifts are spread over the whole 550–250 cm^{-1} region. It is thus impossible to assign the bands on the basis of more or less localized vibrations of TeO_6 , TiO_6 (or SnO_6), and LiO_6 octahedra.

Nevertheless, an interesting feature is the great sharpness of the bands of $\text{Li}_2\text{SnTeO}_6$, to be compared with the very broad pattern given by LiCoTiSbO_6 (Fig. 1). Ac-

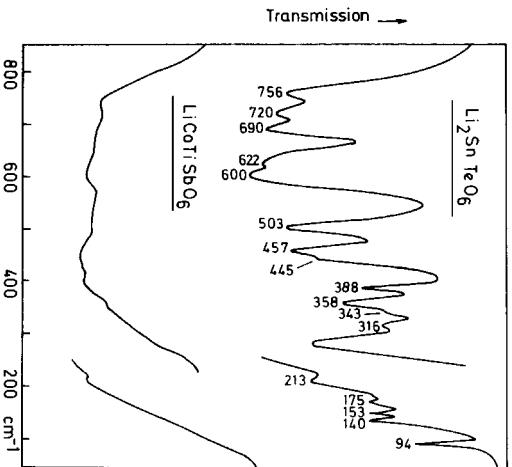


Fig. 1. Compared IR spectra of $\text{Li}_2\text{SnTeO}_6$ (fully ordered distribution of the cations) and LiCoTiSbO_6 (also LiSbO_3 structure, but with Li-Co and Ti-Sb disordering).

ording to its X-ray powder diagram (4) this latter compound also has the LiSbO_3 type structure, but with a *disordered* cation distribution, which is responsible for the broadness of the IR spectrum. The sharpness of the $\text{Li}_2\text{SnTeO}_6$ spectrum points to a fully ordered distribution of the cations, which, in this particular case, could not be deduced from the diffraction data.

Discussion

Description of the LiSbO_3 Structure

The idealized LiSbO_3 structure may be described as a hexagonal close packing of oxygen with $\frac{2}{3}$ of the octahedral sites filled with Li and Sb. Although the polyhedral linkage shows a 3D character, the distribution of cations, i.e., the two cationic sublattices, are of low dimensionality: 1D. As proposed earlier (7) octahedral ribbons run along $\|100\|$ (Fig. 2). SbO_6 units form a string of staggered octahedra, through skew edge-sharing (8). These mixed octahedral ribbons are further connected by opposite face-sharing of all the LiO_6 octahedra in such a way that 1D Li columns are created along $\|010\|$ (Fig. 3). Moreover, that stacking of octahedral ribbons leads to the existence of small tunnels running along $\|100\|$.

Ordering Phenomena

As LiSbO_3 , to our knowledge, is a unique example among the ABO_3 oxides, no order phenomena have been reported until now. Thus, the order evidenced from the structure determination of $\text{Li}_2\text{TiTeO}_6$ (Fig. 2) is especially interesting to analyze. As for the recently reported (1) mixed tellurates $\text{Li}_2\text{Zr}(\text{Hf})\text{TeO}_6$ belonging to the corundum family, the ordering phenomenon in the LiSbO_3 type structure originates in the double substitution $2\text{Sb}^{\text{V}} \rightarrow \text{Ti}^{\text{IV}} + \text{Te}^{\text{VI}}$; more precisely, it is related to the introduction of hexavalent tellurium.

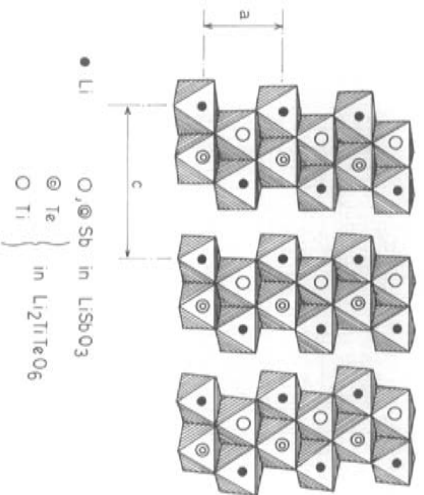


Fig. 2. Octahedral ribbons in the LiSbO_3 type structure at the $y = 0$ level: Ti/Te order in $\text{Li}_2\text{TiTeO}_6$.

One can propose an explanation for such an ordering phenomenon, taking into account the increase of repulsive $M \dots M$ forces in $\text{Li}_2\text{TiTeO}_6$ with respect to LiSbO_3 . We must keep in mind the main result of the analysis of repulsive $M \dots M$ forces developed for the Zr(Hf)/Te order in $\text{Li}_2\text{Zr(Hf)TeO}_6$ (1). A decrease of repulsive forces, compared to the LiNbO_3 type structure, is observed only if there are no neighboring TeO_6 octahedra in the same layer or in two adjacent layers. Similarly, the ordering phenomenon observed for $\text{Li}_2\text{TiTeO}_6$ shows the lack of directly TeO_6 linked octahedra in the same ribbon and between two adjacent ribbons (Figs. 2 and 3). Finally, it is worth noting that in the two structural types, LiNbO_3 and LiSbO_3 , the $M^{\text{IV}}/\text{Te}^{\text{VI}}$ order phenomenon is related to the same geometrical arrangement of the nearest TeO_6 octahedra:

(i) in a ribbon, $\text{Li}_2\text{TiTeO}_6$ (Fig. 2), or in a layer, $\text{Li}_2\text{ZrTeO}_6$ (Fig. 4a), the two closest TeO_6 octahedra are connected through skew-edge sharing of another TiO_6 or LiO_6 octahedron, respectively.

(ii) stacking ribbons or layers leads to nearest TeO_6 octahedra facing each other across a tunnel, $\text{Li}_2\text{TiTeO}_6$ (Fig. 3), or

across an octahedral window, $\text{Li}_2\text{ZrTeO}_6$ (Fig. 4b). Consequently, the corresponding (Te-Te) distances are very similar in the two cases:

$$d_{\text{min}}(\text{Te-Te}) \begin{cases} \text{Li}_2\text{TiTeO}_6 \rightarrow \begin{cases} \text{in a ribbon across a tunnel} \\ a \approx 5.07 \text{ \AA} & b \approx 4.9 \text{ \AA} \end{cases} \\ \text{Li}_2\text{ZrTeO}_6 \rightarrow \begin{cases} \text{in a layer} \\ a \approx 5.17 \text{ \AA} & c/3 \approx 4.6 \text{ \AA}. \end{cases} \end{cases}$$

Summarizing these features, it can be observed that the $M^{\text{IV}}/\text{Te}^{\text{VI}}$ ordering phenomena are solved in a rather similar way in the LiNbO_3 and the LiSbO_3 type structures, leading to the same arrangement of the nearest TeO_6 octahedra. The occurrence of either structure (LiNbO_3 or LiSbO_3) mainly depends on both geometrical and bonding problems related to the nature of M . A decrease of the M^{IV} cation size and of its ionic character, as observed for $\text{Zr}^{\text{IV}}(\text{Hf}) \rightarrow \text{Ti}^{\text{IV}}$, stabilizes the LiSbO_3 type structure. From this, it is also likely that an ordered LiSbO_3 structure for $\text{Li}_2\text{SnTeO}_6$ is found.

Conclusion

The new mixed tellurates $\text{Li}_2\text{TiTeO}_6$ and $\text{Li}_2\text{SnTeO}_6$ are structurally related to LiSbO_3 . The main feature, evidenced from the X-ray study, concerns $\text{Li}_2\text{TiTeO}_6$: an

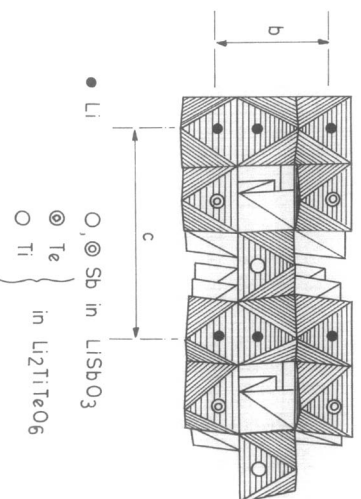


Fig. 3. Face-sharing of LiO_6 octahedra in LiSbO_3 and $\text{Li}_2\text{TiTeO}_6$.

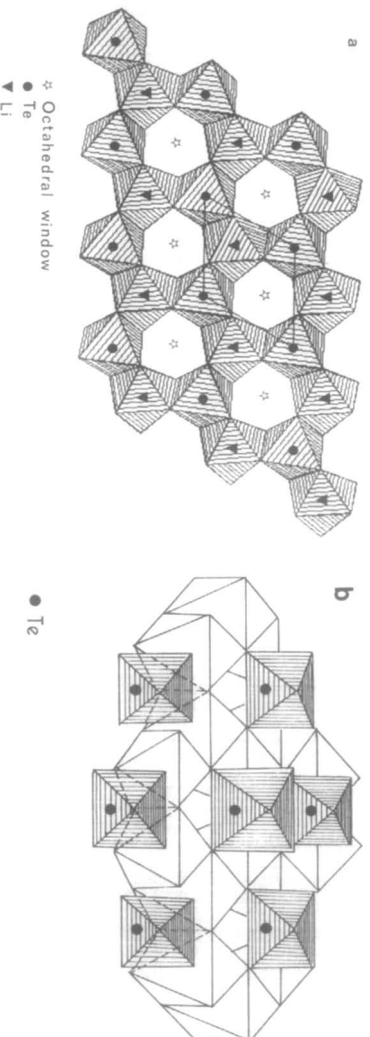


FIG. 4. (a) Octahedral layer in the corundum-like structure of $\text{Li}_2\text{ZrTeO}_6$. (b) TeO_6 octahedra facing each other across octahedral windows in $\text{Li}_2\text{ZrTeO}_6$.

additional 1/1 ordering in the distribution of the (Ti^{IV} , Te^{VI}) pair occurs over the Sb^{V} sites. The existence of a similar $\text{Sn}^{\text{IV}}/\text{Te}^{\text{VI}}$ ordering in $\text{Li}_2\text{SnTeO}_6$, deduced from the IR spectra, must be confirmed by a further neutron diffraction study.

The outstanding influence of Te^{VI} to give ordering in octahedral structures is once more established. Moreover, the comparison of the (Ti^{IV} , Te^{VI}) distribution in the LiSbO_3 and in the corundum ($M^{\text{IV}} = \text{Zr}$, Hf) type structures points to a rather strong similarity in the geometrical arrangement of nearest TeO_6 octahedra. This result leads us to consider the $\text{Te}^{\text{VI}} \dots \text{Te}^{\text{VI}}$ repulsions as the driving forces in the existence of such ordering phenomena.

References

1. J. CHOISNET, A. RULMONT, ET P. TARTE, *J. Solid State Chem.* **75**, 124 (1988).
2. S. C. AVRAHAMIS, J. M. REDDY, ET J. L. BERNSTEIN, *J. Phys. Chem. Solids* **27**, 997 (1966).
3. M. EDSTRAND ET N. INGRI, *Acta Chem. Scand.* **8**, 1021 (1954).
4. P. TARTE ET M. GABELICA-ROBERT, *C.R. Acad. Sci. Paris C* **296**, 261 (1983).
5. C. C. PHAM, J. CHOISNET, ET B. RAVEAU, *Bull. Acad. Roy. Belg. Cl. Sc.* **61**, 473 (1975).
6. E. F. BERTAUT, *C.R. Acad. Sci. Paris C* **230**, 213 (1950).
7. P. LACORRE, M. HERVIEU, ET B. RAVEAU, *Mat. Res. Bull.* **19**, 693 (1984).
8. A. F. WELLS, "Structural Inorganic Chemistry," Univ. Press (Clarendon), London/New York (1984).