JOURNAL OF SOLID STATE CHEMISTRY **130,** 322–326 (1997)
ARTICLE NO. SC977397

LETTER TO THE EDITOR

Low-Temperature Triclinic Distortion in NASICON-Type $LiSn_2(PO_4)_3$

Juan E. Iglesias,[1] Jesús Sanz, Ana Martínez-Juárez, and José M. Rojo

Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain

Communicated by J. B. Goodenough March 3, 1997; accepted March 18, 1997

The triclinic nature of the low-temperature modification of $LiSn_2(PO_4)_3$, heretofore considered as monoclinic, has been proved by detailed indexing of its X-ray diffraction powder pattern. The triclinic character of most low-temperature polymorphs of NASICON-type $LiMe_2^{IV}(PO_4)_3$ is tentatively hypothesized, from this evidence and additional indications. © **1997 Academic Press**

The compound $LiSn_2(PO_4)_3$ is dimorphic: it has a high-temperature form (1–3), isostructural with the rhombohedral, $R\overline{3}c$, NASICON aristotype (4–6), and a low-temperature, low-symmetry modification, stable in pure form at room temperature. The two phases coexist in the ranges 100–150°C and 60–10°C, and they transform into each other through a first-order phase transition showing a hysteresis cycle in temperature (3).

The low-temperature phase was characterized as rhombohedral, different from the NASICON type, but several lines in the powder X-ray diffraction pattern, among them some prominent ones, were left unindexed (2). The phase was subsequently identified as monoclinic, independently by two research groups (7–8), on the basis of very similar monoclinic C-cells, in terms of which the whole powder pattern could be accounted for. The lattice parameters were (7) $a = 14.666(8)$, $b = 8.430(3)$, $c = 8.911(5)$ Å, $\beta = 123.15(3)°$, and (8) $a = 14.6656(7)$, $b = 8.4052(4)$, $c = 8.8933(4)$ Å, $\beta = 122.986(4)°$. These sets of parameters only differ from one another by about 0.2%, once they are corrected for differences in the assumed values for the wavelength, and are almost identical when their specified errors are taken into account. Systematic absences (8), hkl, $h + k = 2n$; $h0l$, $l = 2n$, indicated space groups Cc and $C2/c$, both subgroups of, $R\overline{3}c$, as possible; space group Cc was chosen as the most likely on the basis of NMR evidence, namely the presence of three ^{31}P equally intense lines and two equal ^{119}Sn lines, instead of two and one, respectively, which would have indicated $C2/c$ (8).

We have studied recently (9) a low-temperature form of $LiHf_2(PO_4)_3$, stable below $\approx -40°C$, which is, again, a low symmetry distortion of a high-temperature, $R\overline{3}c$, NASICON-type structure. In this case it was however clear, even at the medium angular resolution of our low-temperature X-ray powder diffraction experiment, that this phase was triclinic. In fact, in the usual rhombohedral $R\overline{3}c \rightarrow$ monoclinic $C2/c$ transformation, the reflection 024_{rh}, which is strong and free of overlap with other reflections, splits into $400_{mon} + \overline{2}22_{mon} + 22\overline{2}_{mon}$; the last two reflections are symmetry equivalent in a monoclinic lattice, and hence 024_{rh} must give two reflections, one twice as intense as the other, if the rhombohedral structure distorts to a monoclinic geometry. However three equally intense peaks could be seen, and from this the first few lines of the pattern could be indexed in terms of a triclinic cell (9). This result has been confirmed from neutron diffraction data (10).

From the above, we felt compelled to reexamine low-temperature $LiSn_2(PO_4)_3$ under conditions of enhanced resolution. To this end, we measured a new diffractometer trace for $12° \leq 2\theta \leq 70°$ in a Philips X'pert diffractometer, fitted with a Ge(111) incident beam monochromator of the Johansson symmetric type, using $CuK\alpha_1$ radiation ($\lambda = 1.5405981$ Å). Previous data indicated that strain-free, well-crystallized materials could give around 0.06° for FWHM, using moderate values of the equatorial divergence. The data were therefore taken with a 0.5° divergence slit, an antiscatter slit of 1°, a receiving slit of 0.01°, and a set of Soller slits with an axial divergence of $\approx 1.1°$ in the diffracted beam path. The usual $\theta/2\theta$ mode was used, and intensity was counted at steps of 0.02° for 10 s. The flat sample was spun around its normal at about 2 Hz. A second trace was obtained under the same conditions and reduced 2θ domain, with a small amount of NIST Si standard ($a = 5.430940$ Å for the wavelength quoted above) intermixed with the sample material for calibration purposes. Peak positions were determined by hand, with the help of the

---

[1] To whom all correspondence should be addressed.

0022-4596/97 $25.00

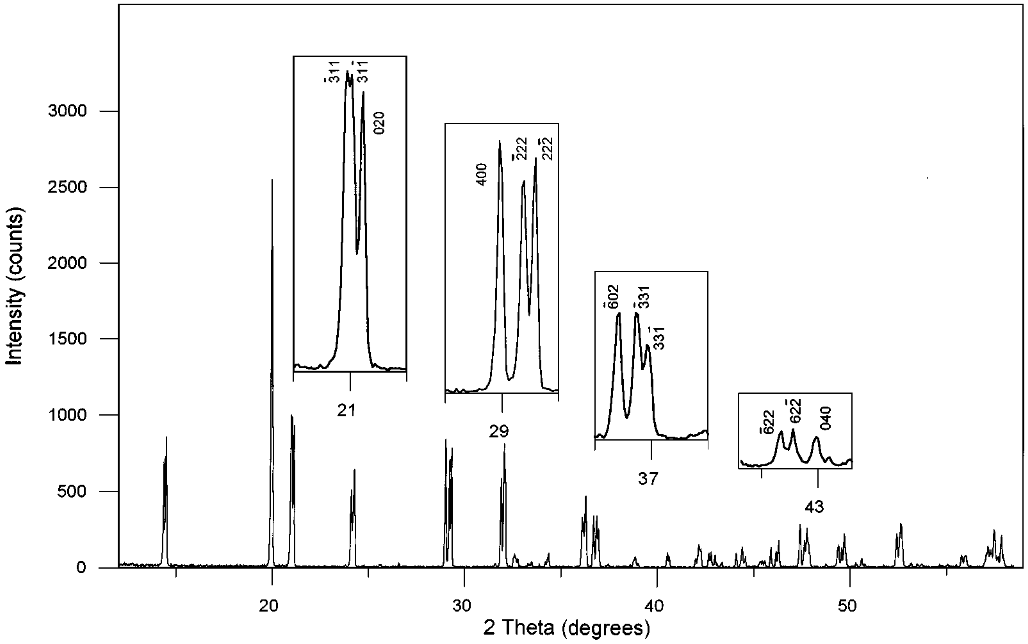

FIG. 1. Room temperature X-ray diffraction powder pattern of $LiSn_2(PO_4)_3$. The insets, each covering an angular domain of 1° in 2θ, correspond to splittings from parent reflections 110_{rh}, 024_{rh}, 300_{rh}, 220_{rh}; they are drawn with an arbitrary common intensity scale, but the first two have been shrunk by about 20% in intensity, for clarity.

diffractometer standard software. The trace obtained is in Fig. 1.

The indexing was carried out by trial and error, starting from the group of three peaks at 2θ around 29°, deriving from 024_{rh}, which were assigned Miller indices 400, $\bar{2}22$, and $22\bar{2}$; the first orders of these were consequently indexed. Next, we looked for splitting of 110_{rh} at around $2\theta \approx 21°$, as this reflection is also overlap-free and should give rise to 020, $\bar{3}11$, $31\bar{1}$. The reflection was clearly split into three peaks (see inset in Fig. 1). At this point we had six independent equations to determine the six independent lattice parameters in the triclinic system. The remaining reflections were added in small groups, performing least squares calculations to constantly refine the initial parameters. For each family of reflections coming from each measurable reflection in the pattern of the rhombohedral parent phase, care was exercised that all members could be accounted for, either as clearly resolved peaks (see two more instances of resolved pairs in the insets of Fig. 1), or if unresolved, by assigning the same observed value to several predicted reflections which were expected to be of about equal intensity. Whenever the last case occurred, the unit weight assigned in all refinements to uniquely resolved reflections was split among the various reflections sharing the same observed value. A number of weak observations that could not be indexed under the above requisites were satisfactorily assigned once the reflections derived from $R\bar{3}c$ space group extinctions were allowed in the indexing; all of them are weak and are duly marked in Table 1, where the indexed pattern is shown. In all, only three very small peaks at $2\theta = 26.59°$ (Int = 2), 33.86° (Int = 1), and 51.78° (Int < 1), identified (11) as the three strongest reflections of tetragonal SnO_2 (cassiterite), were considered impurity lines and left unindexed. The lattice parameters of a nonconventional C-centered triclinic cell obtained from least squares refinement with all data presented in Table 1 are: $a = 14.680(1)$, $b = 8.4134(4)$, $c = 8.9003(8)$ Å, $\alpha = 89.799(6)$, $\beta = 122.976(6)$, $\gamma = 90.166(6)°$. The reduced Niggli cell was obtained following a published algorithm (12): $a_N = 8.4134(8)$, $b_N = 8.449(1)$, $c_N = 8.9003(8)$ Å, $\alpha_N = 118.104(8)$, $\beta_N = 90.201(9)$, $\gamma_N = 119.693(8)°$. The transformation matrix from the conventional to the Niggli cell is $(0\,\bar{1}\,0/\tfrac{1}{2}\tfrac{1}{2}0/0\,0\,1)$. Miller indices referred to the Niggli cell are also furnished in Table 1.

The quality of the indexing can be judged through several estimators. First, it can be seen that $|\Delta(2\theta)| \leq 0.031°$ for all reflections; in fact, $|\Delta(2\theta)| \leq 0.02°$ for about 94% of the computed reflections and $|\Delta(2\theta)| \leq 0.01°$ for about 64% of these. If a sort of R factor is defined, $R = \sum|2\theta_{obs} - 2\theta_{calc}|/\sum 2\theta_{obs}$, then $R = 0.00022$. The de Wolff (13) figures of merit are

$$M(20) = 55(33) \quad (0.000028, 24(40)),$$

$$M(30) = 34(25) \quad (0.000030, 42(58)),$$

$$M(50) = 24(17) \quad (0.000039, 69(95)),$$

where the first value quoted for each index has been calculated by reckoning only those reflections derived from

TABLE 1
X-Ray Powder Diffraction Pattern for Triclinic Low Temperature $LiSn_2(PO_4)_3$

#	$2\theta_{obs}$	I/I_o	d_{obs} (Å)	h_C	k_C	l_C	h_N	k_N	l_N	$\Delta(2\theta)$
1	14.371	28	6.16	2	0	0	0	1	0	−0.002
2	14.471	34	6.12	−1	1	1	−1	0	1	0.003
[a]3	14.527	16	6.09	1	1	−1	1	−1	1	0.006
4	19.935	100	4.45	1	1	1	−1	1	1	0.009
				−1	1	−1	1	0	1	−0.011
[a]5	19.998	55	4.44	−2	0	2	0	−1	2	0.007
[b]6	20.968	38	4.23	−3	1	1	−1	−1	1	0.009
7	21.011	38	4.22	3	1	−1	1	−2	1	−0.002
8	21.104	36	4.21	0	2	0	−2	1	0	0.002
9	23.801	1	3.735	0	0	2	0	0	2	−0.014
10	24.100	20	3.690	−3	1	0	1	1	0	0.008
				3	1	0	−1	2	0	−0.015
[c]11	24.197	15	3.675	−3	1	2	−1	−1	2	0.010
12	24.261	25	3.666	0	2	1	−2	1	1	0.020
				3	1	−2	1	−2	2	0.003
[a]13	24.295	14	3.661	0	2	−1	2	−1	1	0.005
[e]14	24.758	1	3.593	2	2	−1	2	−2	1	0.011
[b]15	25.565	1	3.482	−4	0	2	0	−2	2	−0.007
16	25.628	1	3.473	−2	2	0	2	0	0	0.017
				2	2	0	−2	2	0	−0.012
17	28.976	33	3.079	4	0	0	0	2	0	−0.003
18	29.182	29	3.058	−2	2	2	−2	0	2	0.008
19	29.282	29	3.048	2	2	−2	2	−2	2	0.001
[e]20	31.548	1	2.8336	2	2	1	−2	2	1	0.013
				−2	2	−1	2	0	1	−0.002
21	31.857	23	2.8068	3	1	1	−1	2	1	0.001
				−3	1	−1	1	1	1	0.000
22	32.009	32	2.7938	−3	1	3	−1	−1	3	0.005
23	32.071	25	2.7886	0	2	−2	2	−1	2	0.006
[c]24	32.515	3	2.7515	−5	1	2	−1	−2	2	0.001
				−4	2	1	−2	−1	1	−0.023
25	32.568	3	2.7472	5	1	−2	1	−3	2	−0.012
[a]26	32.630	2	2.7421	4	2	−1	2	−3	1	0.009
27	32.728	2	2.7341	−1	3	0	−3	1	0	0.013
				1	3	0	−3	2	0	−0.004
28	33.260	1	2.6916	5	1	−1	1	−3	1	0.016
29	33.445	1	2.6771	4	2	−2	2	−3	2	0.000
				−1	3	1	−3	1	1	−0.002
30	34.184	2	2.6209	2	0	2	0	1	2	0.012
[c]31	34.279	3	2.6138	−1	1	3	−1	0	3	−0.004
32	34.337	4	2.6096	1	1	−3	1	−1	3	−0.005
[b]33	36.108	13	2.4855	−4	2	0	−2	−1	0	0.005
34	36.159	11	2.4821	4	2	0	−2	3	0	0.014
				−5	1	3	−1	−2	3	−0.022
35	36.284	19	2.4739	5	1	−3	1	−3	3	0.026
				1	3	1	−3	2	1	0.004
				−1	3	−1	3	−1	1	−0.031
36	36.700	13	2.4468	−6	0	2	0	−3	2	−0.003
37	36.861	13	2.4365	−3	3	1	−3	0	1	−0.004
38	36.958	10	2.4303	3	3	−1	3	−3	1	−0.003
[e]39	37.334	< 1	2.4067	−2	2	3	−2	0	3	−0.013
[e]40	37.460	1	2.3989	2	2	−3	2	−2	3	−0.006
[e]41	38.623	1	2.3293	−6	0	1	0	−3	1	0.004
[c,e]42	38.772	2	2.3207	−6	0	3	0	−3	3	−0.004
[e]43	38.826	3	2.3176	−3	3	0	3	0	0	−0.011
[e]44	38.865	3	2.3153	−3	3	2	−3	0	2	−0.003
[e]45	38.993	1	2.3080	3	3	−2	3	−3	2	−0.014
[c]46	40.483	3	2.2264	2	2	2	−2	2	2	−0.006
47	40.528	4	2.2241	−2	2	−2	2	0	2	−0.003

TABLE 1—*Continued*

#	$2\theta_{\mathrm{obs}}$	I/I_{o}	d_{obs} (Å)	h_{C}	k_{C}	l_{C}	h_{N}	k_{N}	l_{N}	$\Delta(2\theta)$
48	40.607	3	2.2199	−4	0	4	0	−2	4	−0.018
49	41.985	2	2.1502	3	1	2	−1	2	2	0.012
				−3	1	−2	1	1	2	−0.004
50	42.139	6	2.1427	−3	1	4	−1	−1	4	−0.024
				−1	1	−3	1	0	3	−0.006
51	42.244	5	2.1376	3	1	−4	1	−2	4	0.008
				−2	0	4	0	−1	4	0.018
52	42.662	4	2.1176	−6	2	2	−2	−2	2	−0.001
53	42.774	4	2.1123	6	2	−2	2	−4	2	−0.003
54	42.970	3	2.1032	0	4	0	−4	2	0	0.004
55	43.085	1	2.0978	−4	2	−1	2	1	1	−0.004
				4	2	1	−2	3	1	−0.011
56	43.260	< 1	2.0897	1	3	2	−3	2	2	0.019
57	43.328	1	2.0866	−1	3	−2	3	−1	2	0.014
				5	1	−4	1	−3	4	0.007
58	44.079	4	2.0528	6	0	0	0	3	0	−0.007
[d] 59	44.323	2	2.0420	3	3	1	−3	3	1	−0.012
				−3	3	−1	3	0	1	−0.014
60	44.365	4	2.0402	−6	0	4	0	−3	4	−0.001
61	44.395	5	2.0389	−3	3	3	−3	0	3	0.003
62	44.568	3	2.0314	3	3	−3	3	−3	3	0.008
63	45.328	2	1.99908	−5	3	1	−3	−1	1	0.005
				7	1	−3	1	−4	3	−0.019
64	45.432	2	1.99475	5	3	−1	3	−4	1	0.002
65	45.540	2	1.99027	−2	4	0	−4	1	0	0.021
				2	4	0	−4	3	0	−0.014
66	45.882	5	1.97623	−5	1	−1	1	2	1	−0.001
				5	1	1	−1	3	1	−0.009
67	46.159	4	1.96501	−1	3	3	−3	1	3	0.004
				−4	2	4	−2	−1	4	0.015
[c,e]68	46.270	5	1.96055	−1	1	4	−1	0	4	0.010
69	46.301	7	1.95931	1	3	−3	3	−2	3	0.009
				1	1	−4	1	−1	4	−0.018
				4	2	−4	2	−3	4	0.012
70	47.378	11	1.91725	4	0	2	0	2	2	0.008
				−7	1	1	−1	−3	1	−0.001
71	47.620	7	1.90807	−2	2	4	−2	0	4	0.015
				−5	3	3	−3	−1	3	−0.017
72	47.736	10	1.90371	2	2	−4	2	−2	4	0.007
				−2	4	2	−4	1	2	−0.010
73	47.838	6	1.89989	5	3	−3	3	−4	3	0.017
74	47.890	4	1.89794	2	4	−2	4	−3	2	0.003
75	48.730	< 1	1.86717	0	0	4	0	0	4	−0.015
76	49.348	5	1.84523	−6	2	0	2	2	0	0.008
77	49.389	6	1.84379	6	2	0	−2	4	0	0.000
78	49.547	5	1.83828	−6	2	4	−2	−2	4	0.002
[c]79	49.645	5	1.83488	0	4	2	−4	2	2	−0.016
80	49.683	9	1.83357	6	2	−4	2	−4	4	−0.016
81	49.774	4	1.83043	0	4	−2	4	−2	2	0.008
82	50.290	1	1.81285	8	0	−2	0	−4	2	−0.005
83	50.582	2	1.80307	−4	4	2	−4	0	2	−0.003
84	50.749	< 1	1.79753	4	4	−2	4	−4	2	−0.004
85	52.396	8	1.74483	4	2	2	−2	3	2	0.009
				−4	2	−2	2	1	2	−0.010
86	52.548	9	1.74014	1	3	3	−3	2	3	0.012
87	52.619	12	1.73796	−5	1	5	−1	−2	5	0.009
				−1	3	−3	3	−1	3	−0.019
[a]88	52.705	7	1.73533	5	1	−5	1	−3	5	0.012
89	53.154	1	1.72172	−7	1	0	1	3	0	0.024
				7	1	0	−1	4	0	−0.003

TABLE 1—*Continued*

#	$2\theta_{\text{obs}}$	I/I_o	d_{obs} (Å)	h_C	k_C	l_C	h_N	k_N	l_N	$\Delta(2\theta)$
[b] 90	53.471	1	1.71226	-5	3	4	-3	-1	4	0.007
				3	1	3	-1	2	3	-0.019
91	53.518	<1	1.71087	-3	1	-3	1	1	3	0.002
				-2	4	3	-4	1	3	-0.010
[b] 92	53.664	<1	1.70656	5	3	-4	3	-4	4	-0.007
93	53.712	<1	1.70515	2	4	-3	4	-3	3	0.004
94	54.650	<1	1.67808	-8	2	3	-2	-3	3	0.008
95	54.776	<1	1.67451	8	2	-3	2	-5	3	0.000

Note. Miller indices with subscript C refer to the C-centered cell; those with subscript N refer to the Niggli cell.

[a] Shoulder of previous reflection.

[b] Barely resolved doublet.

[c] Shoulder of following reflection.

[d] Complex shoulder of following reflection.

[e] Parent reflection in $R\bar{3}c$ is a space group extinction.

nonforbidden reflections in the parent $R\bar{3}c$ structure; the second value (in parentheses) has been calculated for a general triclinic lattice. The expression in parentheses following each M value contains the average error in $\sin^2\theta$ and the expected number of reflections in the appropriate domain for each of the two situations referred to above.

We have therefore proved that room-temperature $LiSn_2(PO_4)_3$ is indeed triclinic, although the deviation from C-lattice monoclinic is quite small. Moreover, from our NMR observations (8), mentioned above, we can conclude that the space group must be $C\bar{1}$ ($P\bar{1}$ if referred to a conventional cell), since the number of crystallographically independent P and Sn atoms coincides with the number of NMR lines observed; there would be twice as many lines if the group were $C1$. We have also a preliminary qualification of low-temperature $LiHf_2(PO_4)_3$ as also triclinic (9), and our old data on room temperature $LiZr_2(PO_4)_3$ show also, when looked at with the benefit of hindsight, the telltale splitting of 024_{rh}, albeit not as clearly as that in the pattern of low-temperature $LiHf_2(PO_4)_3$. It may well be that all low-temperature forms in NASICON-type $LiMe_2^{IV}(PO_4)_3$ orthophosphates are triclinic rather than monoclinic, as they have customarily been considered. We cannot advance anything of the sort for Na compounds; there are several well-refined structures (14–17) for these, all of them monoclinic, so the triclinic distortion we observe could be a characteristic trait of Li compounds exclusively.

REFERENCES

1. R. Perret and A. Boudjada, *C.R. Acad. Sci. Paris* **282,** C-245 (1976).
2. J.-M. Winand, A. Rulmont, and P. Tarte , *J. Solid State Chem.* **93,** 341 (1991).
3. A. Martínez-Juárez, J. M. Rojo, J. E. Iglesias, and J. Sanz, *Chem. Mater.* **7,** 1857 (1995).
4. L. Hagman and P. Kierkegaard, *Acta Chem. Scand.* **22,** 1822 (1968).
5. H. Y.-P. Hong, *Mater. Res. Bull.* **11,** 173 (1976).
6. J. B. Goodenough, H. Y.-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.* **11,** 203 (1976).
7. J. Angenault, J. C. Couturier, J. P. Souron, D. Siliqi, and M. Quarton, *J. Mater. Sci. Lett.* **11,** 1705 (1992).
8. A. Martínez, J. M. Rojo, J. E. Iglesias, J. Sanz, and R. Rojas, *Chem. Mater.* **6,** 1790 (1994).
9. M. A. Paris, A. Martínez-Juárez, J. E. Iglesias, J. M. Rojo, and J. Sanz, submitted for publication.
10. E. R. Losilla, M. A. G. Aranda, M. Martínez-Lara, and S. Bruque, preprint, 1997.
11. G. McCarthy and J. Welton, *Powder Diff.* **4,** 156 (1989); ICDD-Card 41-1445.
12. I. Krivý and B. Gruber, *Acta Crystallogr. A* **32,** 297 (1976).
13. P. M. de Wolff, *J. Appl. Crystallogr.* **1,** 108 (1968).
14. P. R. Rudolf, M. A. Subramanian, A. Clearfield, and J. D. Jorgensen, *Mater. Res. Bull.* **20,** 643 (1985).
15. P. R. Rudolf, A. Clearfield, and J. D. Jorgensen, *Solid State Ionics* **21,** 213 (1986).
16. J. P. Boilot, G. Collin, and Ph. Colomba, *Mater. Res. Bull.* **22,** 669 (1987).
17. P. R. Rudolf, A. Clearfield, and J. D. Jorgensen, *J. Solid State Chem.* **72,** 100 (1988).