

NOTES

Electron Diffraction from LaF₃ Single Crystals

The Tysonite Structure Problem

There have been several previous reports (1-8) on studies of the LaF₃-type or tysonite structure, and the problem has been reviewed comprehensively in Gmelin (9). Nevertheless, some uncertainties remain as to the size of the unit cell, the space group, and the F-atom positions. All authors are in general agreement over the metal-atom positions. All authors but Schlyter (3) have taken $Z = 6$ on the basis of the diffraction evidence (Schlyter found $Z = 2$), but the choice of the larger cell is determined by the presence of a very few very weak superstructure reflections (1, 2, 4-8, 10). Mansmann (4) has argued that, having regard to the strong scattering power of La and his use of Cu radiation, Schlyter would not have observed these. However, this argument is weak since others (1, 2, 7, 10) have in fact observed them with Cu radiation. The relationship between these two hexagonal or trigonal cells is shown in Fig. 1.

The various space groups reported for the $Z = 6$ cell are $P6_3/mcm$ (1, 2), $P\bar{3}c1$ (4-6), and $P6_3cm$ (7). The space group chosen by Schlyter was $P6_3/mmc$ for the $Z = 2$ cell. Cheetham and Fender (8), using powder neutron diffraction and profile analysis techniques, have confirmed the existence of the $Z = 6$ cell for their sample, and narrowed the choice of space group to either $P\bar{3}c1$ or $P6_3cm$: no satisfactory refinement was obtained in $P3_1/mcm$. In the absence of both a piezo-

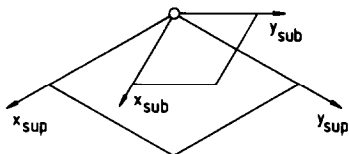


FIG. 1. Relationship between the subcell ($Z = 2$) and the supercell ($Z = 6$) of the LaF₃ structure ($a_{sup} = \sqrt{3} \cdot a_{sub}$ and $c_{sup} = c_{sub}$).

and a pyroelectric (6) effect, the centrosymmetric space group $P\bar{3}c1$ then remains as the more likely.

No single-crystal electron diffraction data on LaF₃ or its isotypes have been published, in spite of the fact that this technique is especially powerful for the solution of problems relating to the geometry of superstructure cells (11). This work reports such data on LaF₃.

Experimental

LaF₃ was prepared from La₂O₃ (99.99%, Auer-Remy KG, Hamburg). The oxide was first dissolved in concentrated HCl. LaF₃ was precipitated with 40% HF solution, then dried in air at 120°C. This product was placed in a vitreous-carbon boat inside a tube of the same material and heated for several days at 900°C in a stream of high-purity N₂ and water-free HF. It was then cooled *in situ* to room temperature over a period of several hours.

The Guinier powder patterns of the well-crystallized LaF₃ so obtained showed clearly the few weak reflections indicative of the existence of the $Z = 6$ cell, whose parameters were previously determined (12) as $a = 7.1871(4)$ Å, $c = 7.3501(5)$ Å, and $V = 328.80(4)$ Å³. Electron diffraction patterns from LaF₃ single crystals with diameter less than ~ 3500 Å were obtained with an AEI-EM 802 electron microscope fitted with a double tilt ($\pm 30^\circ$, $\pm 5^\circ$) and rotation (360°) goniometer stage. The operating voltage was 100 kV.

Results and Discussion

Numerous reciprocal-lattice sections were photographed, some being single sections from different, randomly chosen crystals, while others constituted sets obtained from one single crystal in several different orientations.

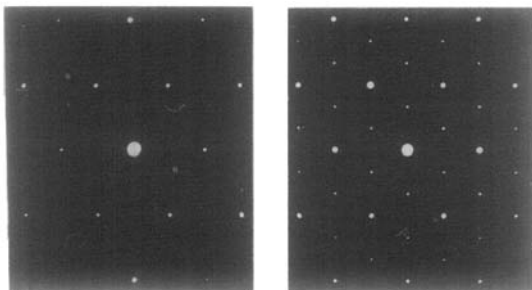


FIG. 2. Electron diffraction photographs of the [001] zones of the sublattice (left) and the superlattice (right) of different LaF_3 single crystals.

Analysis confirmed the presence of the superlattice cell with $Z = 6$, and the observed systematic absences corresponded to those for any of the three previously reported space groups. However, it is impossible on the evidence obtained here to distinguish between these. What is interesting and significant is that not all crystals examined showed this superlattice. Some were found whose reciprocal lattice corresponded to the structure with $Z = 2$, reported by Schlyter, and these contained only the so-called subcell reflections. Figure 2 shows photographs of the [001] zones of the sublattice and superlattice respectively, and Fig. 3 shows the relationship between the two in reciprocal space (cf. Fig. 1). Moreover, for small crystals ($<1000 \text{ \AA}$ in diameter) initially showing superstructure reflections, normal beam irradiation led to the disappearance of these reflections, and it is clear that disordering of the superlattice can occur. On the other hand, larger crystals exhibiting superstructure reflections were quite stable in the beam for a period of several hours. No

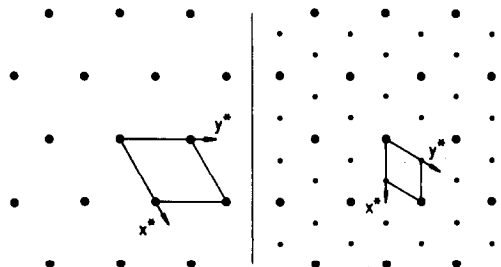


FIG. 3. Relationship between the sublattice (left) and the superlattice (right) of LaF_3 in reciprocal space.

evidence of chemical degradation (as occurs with rare-earth oxide-fluorides (13)) was observed.

Apparently LaF_3 can crystallize in at least two different modifications (space groups $P\bar{3}c1$ and $P6_3/mmc$), the first corresponding to an ordering and a lower symmetry of the anion array (the supercell with $Z = 6$), and the second in which the anion array is less well ordered and has a higher symmetry (the subcell with $Z = 2$). This behavior correlates well with the unusually high F^- -ion mobility at room temperature (14–16).

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Received September 16, 1977