Crystal structure and microstructure of some \( \text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3 \) by synchrotron X-ray diffraction

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The structure of all materials lies between the idealised crystalline and the completely disordered amorphous state. The knowledge of the real (defective) structure of a material is very important to understand how the material is built and to explain many of its properties. Solid electrolytes are, probably, one of the most evident examples of this. Since mass transport in solids is due to the existence of defects, solid ionic conductors can only exist as real solids. Despite the title materials, \( \text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3 \) being among the best ionic conductors, little attention has been paid to the study of their microstructure. The effects of microstructure on the powder diffraction patterns (either x-ray or neutron data) may indeed be significant. In fact, the broadness of the superlattice reflections in the powder diffraction patterns of many of these oxides can be very pronounced as a consequence of strong microstructure effects. Thus, in the effort to account for the whole pattern, unrealistic or unnecessarily complex models may be developed for describing the average (ideal) structure of these materials [1-4]. At this point it must be stressed that real solids are usually very complex; this means that to develop an adequate model it is absolutely necessary to obtain diffraction data of as high as possible resolution and quality on very high quality samples.

Therefore, to deal with the study of the crystal structure of the \( \text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3 \) materials, a view of the whole system must be adopted and the dependence of the microstructure of the samples with the annealing temperature and composition must be considered. The materials chosen for this work have the composition \( \text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3 \) and \( \text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3 \) corresponding to the values \( x=0.07 \) and \( x=0.12 \), respectively. In this paper we study the \( \text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3 \) oxide annealed at 1000°C and quenched from this temperature and the \( \text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3 \) compound treated at two different temperatures, 800°C and 1000°C, and quenched from there.

The crystal structure of materials with complex microstructure effects need to be study by different complementary techniques, which allow to detect and to treat the extended defects present in real solids. SAED and HRTEM results of materials of the \( \text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3 \) system indicate that they have a perovskite-related structure with unit cell dimensions \( \sqrt{2}a_c \times \sqrt{2}a_c \times 2a_p \). Domains with different orientation of the unit cell form all the crystals and the size of the domains depends on the thermal treatment and the composition of the oxides.

These results have led us to consider the microstructure of the materials for determining their crystal structure. In this way, the crystal structure of three representative oxides of the system has been solved from synchrotron X-ray diffraction data (see Fig. 1).
The high resolution of this technique has allowed us to distinguish between the monoclinic symmetry of the La_{0.6}Li_{0.2}TiO_3 quenched from 1000°C and the orthorhombic symmetry of the La_{0.55}Li_{0.35}TiO_3 quenched from 1000 and 800°C. All the materials obey the same octahedral tilting mechanism and ordering of the lanthanum and lithium ions and vacancies occurs along the 2a_p-axis. This ordering depends on both the annealing temperature and the composition of the samples. However, location of the lithium ions must be obtained from neutron diffraction data. Besides, displacements of the titanium ions from the centre of the TiO_6 octahedra are also observed.

We have also determined the average sizes and shapes of the domains of the three samples and we have detected other microstructure effects such as strains and compositional fluctuations, which depend on both the thermal treatment and the sample composition (Fig. 2).

Finally, it must be stressed that microstructural studies have valuable importance for the understanding and the optimisation of the physico-chemical properties of solids. Regarding the lithium ionic conductors La_{2/3-x}Li_{3x}TiO_3, subject of this work, and other related systems [6], we have found that the materials’ performance as lithium conductors seems to be strongly dependent on the exact composition and on the microstructure. The oxides with the highest ionic conductivity in every system are those with 8% of vacancies within the A-sites in the perovskite structure, and formed by microwinned crystals. In this connection, some years ago Harada et al. [7] have been reported that among samples of La_{2/3-x}Li_{3x}TiO_3 of different compositions and thermal histories, those with high lithium content (x>0.09) and annealed and quenched from high temperature (~1350°C) present higher conductivity than those treated at lower temperature (800°C). Interestingly, we have recently shown [6] that the samples with lithium contents corresponding to (x>0.10) annealed and quenched at high temperature present microwins and a very defective microstructure as a consequence of a high density compositional mistakes within the microdomains. Thus, high ionic conductivity in perovskite-like systems seems to be clearly related to the microstructure of the material, which can be modified by adjusting the composition and controlling the thermal treatments the material is submitted to.

References