9. Phase Sequences in Processing

PZT and SBT exist in several different phases. When PZT films are deposited under normal conditions the phase that is formed has the pyrochlore structure. These pyrochlores are generally ferroelectric but only at cryogenic temperatures; thus, they are not useful for room temperature ferroelectric memory devices. The pyrochlores deposited by sputtering, sol–gel spin-on, or other techniques are subsequently subjected to an annealing cycle, either in a furnace (typically an hour at 650°C) or via RTA (Rapid Thermal Annealing), typically for 90 seconds to a maximum temperature of about 800°C. These heat treatments result in 100% of the material being converted to the ferroelectric perovskite phase. Usually this heating process is carried out in an oxygen atmosphere to prevent oxygen loss from the film. The lowest temperature at which 100% of the film has been successfully converted to perovskite is 450°C [334]. Recently it has been suggested [334] that the pyrochlore phase is stabilized by Pb⁴⁺ ions in PZT, and efforts are underway to reduce this Pb⁴⁺ concentration to see if even lower temperature conversion to the perovskite phase is possible.

Fig. 9.1. SrBi₂Ta₂O₉ structure [338, 339]
SBT has a different sequence of phases. As-deposited films have a defective fluorite structure [335]. An ideal fluorite structure would have eightfold coordination of the Ta ion, with eight nearest-neighbour oxygens. The actual structure has octahedral sixfold coordination with two of these eight oxygen ions 'missing'. This fluorite phase is not ferroelectric. It must be heated to convert it to the ferroelectric Aurivillius layer-structure phase shown in Fig. 9.1. As with PZT, the heating can be done by furnace anneal or by RTA. Furnace anneals require a minimum temperature of about 600°C. (Lower values of temperature have been quoted for Plasma-Enhanced Chemical Vapour Deposition – PECVD – or CVD using cyclotron resonance, but the actual surface temperature is difficult to determine in these deposition schemes.) The fact that the processing temperature for SBT is thus about 150°C higher than for PZT is a significant disadvantage in commercializing SBT memories. The main difficulty is that it precludes the use of aluminium metallization for the SBT memory devices.

![Figure 9.2](image.png)

**Fig. 9.2.** EXAFS data for fluorite and Aurivillius phases of SBT [337]

It was proposed [336] that in the intermediate fluorite phase of SBT the Sr, Bi, and Ta ions randomly occupy the M-site of the basic MO$_2$ fluorite structure, despite the fact that their ionic radii and valences are different. This was confirmed [337] by the EXAFS data shown in Fig. 9.2.

The actual structure of SBT or SBN has a slight orthorhombic distortion from the tetragonal structure pictured [338, 339].