Crystal growth, phase stability and structural transition of orthorhombic Sr_2TiO_4

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The ternary system Sr-Ti-O has been subject of strong interest for long time, mainly because of the exciting physics exhibited by $SrTiO_3$. However, the other members of the Ruddlesden-Popper (RP) structural series $Sr_{n+1}Ti_nO_{3n+1}$ have been overlooked, mostly because of the lack of pure and crystalline samples of the compositions with $n \neq \infty$. In this composition range, the phase diagram has not been assessed for decades, and the complex phase equilibria and phase transitions are still to be elucidated. We report the crystallization of the $n = 1$ RP-member Sr_2TiO_4 from the melt, by means of a floating-zone melting and growth, followed by a fast cooling procedure [1]. We successfully stabilized the high-temperature polymorph in a crystalline form, and found that it crystallizes in an orthorhombic space group with a very rare tetrahedral coordination of Ti-atoms. We report its crystal structure (β-K_2SO_4 structure type, $Pna2_1$ space group) as obtained from both powder and single-crystal X-ray diffraction, and the structural transition to the tetragonal RP-polymorph as studied by high-temperature in-situ X-ray diffraction and thermal analysis. A complex reconstructive phase transition occurs between the tetragonal RP compound, with octahedral Ti, and the high-temperature orthorhombic polymorph, with tetrahedral Ti. An orientation relationship is found between the orthorhombic and tetragonal phases during the transition, which suggests that the growth of tetragonal Sr_2TiO_4 might be controlled as well. The orthorhombic Sr_2TiO_4 is an insulator, with a band gap of 3.9 eV and has a large (≈40) dielectric constant, but despite its polar structure does not show any signatures of a ferroelectric order.

[1] D. Pulmannová, C. Besnard, P. Bezdička, M. Hadjimichael, J. Teyssier and E. Giannini. Crystal growth and structure of a high temperature polymorph of Sr_2TiO_4 with tetrahedral Ti-coordination, and transition to the Ruddlesden–Popper tetragonal phase CrystEngComm. 2022;24(20):3731-3740.