Crystal structure of a new polymorph of Sr_2TiO_4 with tetrahedral titanium

D. Pulmannova, C. Besnard, E. Giannini

Univeristy of Geneva, Quai Ernest-Ansermet 24, 1205 Geneva, Switzerland

dorota.pulmannova@unige.ch

Sr_2TiO_4, first member of the Ruddlesden-Popper series $Sr_{n+1}Ti_nO_{3n+1}$, has been long known to undergo a phase transition at 1550 °C. This transition makes the growth of single crystals of this material highly challenging, because it usually breaks the crystal into a periodic array of uneven lamellae. While the low temperature tetragonal phase is widely studied due to its close connection to the famous perovskite $SrTiO_3$, there is little information about the high temperature α-phase, except for an unindexed powder pattern by Drys&Trzebiatowski [1].

We stabilized the high-temperature α-Sr_2TiO_4 crystals by rapid cooling of the incongruent melt from above the liquidus temperature. The α-phase crystallizes in the orthorhombic $Pna2_1$ group with lattice parameters a=14.2901(5) Å b=5.8729(2) Å c=10.0872(3) Å and is isostructural to the orthorhombic forms of Sr_2VO_4 and Sr_2CrO_4 (which belong to the β-K_2SO_4 structure type). Its structure is formed by a complicated framework of large SrO_x polyhedra with tetrahedral cavities occupied by the transition metal. The tetrahedral coordination of Ti^{IV} makes the α-Sr_2TiO_4 quite a rare case among titanate compounds, the only other known example being the barium orthotitanate Ba_2TiO_4 [2].

However, whereas in Ba_2TiO_4 the coordination is tetrahedral in both high- and low-temperature polymorphs and the topotactic relation between the two is known, in the case of Sr_2TiO_4 a transition occurs to the layered Ruddlesden-Popper structure with octahedral titanium coordination.

In this work, we report for the first time the crystal structure of the high-temperature α-phase of Sr_2TiO_4. We elucidate the structural differences between the related compounds and discuss possible mechanism driving the structural transition.

[1] Drys, M., Trzebiatowski, W. (1957). *Roczniki Chemii*. **31**, 489.

[2] Gunter, J., Jameson, G. (1984). *Acta Cryst.* C**40**, 207.

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