A high-temperature diffraction study of the solid solution CaTiOSiO₄-CaTiOGeO₄

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ABSTRACT

The structure of CaTiOGeO₄ (CTGO) has been refined using single crystal X-ray diffraction data. CTGO is isostructural with titanite, CaTiOSiO₄. The displacive $P2_1/a$-$A2$/a phase transition analogous to titanite has been studied by in situ heating X-ray powder diffraction and transmission electron microscopy. The transition is accompanied by the disappearance of superstructure reflections, $k + l = 2n + 1$, which are replaced by diffuse scattering for $T > T_c$. The diffuse scattering is seen as streaks along $b^*$ in high-temperature TEM SAD. Lattice parameters as a function of temperature and composition were determined by X-ray powder diffraction between room temperature and a maximum of 1123 K. Strain analysis of CTGO indicates a transition temperature of $T_c = 588 \pm 4$ K and the additional occurrence of an isosymmetric anomaly at $T_i = 800 \pm 25$ K. There is complete solid-solution along the join CaTiOGe(Si₁₋ₓ)O₄. The lattice parameters across the solid solution vary continuously and the structural phase transitions were identified based on the determination of spontaneous strain associated with the transitions. The $e_{11}$ and $e_{11}$ components dominate the strain tensor. All compositions across the solid solution exhibit close to tricritical behavior and nearly constant scalar strain.

INTRODUCTION

The titanite structure has attracted substantial interest because of its phase transitions, its occurrence as a metamict mineral (Hawthorne et al. 1991), and its crystal chemical relation to the non-linear optical material KTiOPO₄ (KTP) (Kunz et al. 2000). Titanite is a common accessory mineral in a variety of metamorphic and igneous rocks. Crystals with less than 3–4 mol% substitution of Fe and Al for Ti have the space group $A2/a$ whereas those with more than 4 mol% (Al + Fe) have diffuse reflections $h + k = 1$ which become unobservable above 20 mol% substitution as the average structure approaches $A2/a$ symmetry (Higgins and Ribbe 1976; Oberti et al. 1991). The structural framework of titanite is formed by parallel chains of corner-sharing TiO₆ octahedra running along $a$. The parallel strings of octahedra are connected by GeO₄ tetrahedra sharing corners with the TiO₆ octahedra and by Ca in seven-coordination (Speer and Gibbs 1976; Taylor and Brown 1976).

At about $T_c = 487$ K, titanite undergoes a phase transition associated with a displacement of Ti atoms from the center of the TiO₆ octahedron (Ghose et al. 1991; Bismayer et al. 1992). Above the transition temperature the space group is $A2/a$ ($C2/c$) whereas below the space group is $P2_1/a$ ($P2_1/c$) (Taylor and Brown 1976; Ghose et al. 1991). The ordered low-temperature phase is characterized by alternating short and long Ti-O bonds along $[100]$, with a reversed sense of Ti displacement in adjacent octahedral chains. In the $A2/a$-structure Ti is located at the centre of the TiO₆ octahedra. The transition is accompanied by the disappearance of superlattice diffraction maxima with $k + l = 2n + 1$. It is believed that the phase transition at 487 K involves merely a two-dimensional loss of long-range coherence between the off-center dipoles, while the structure remains ordered with respect to the (dynamic) Ti-displacement along individual octahedral chains (Malcherek et al. 2000). True $A2/a$ symmetry is thought to occur via a second, isosymmetric phase transition around $T_i = 825$ K. The first evidence for this second anomaly was obtained from excess birefringence (Bismayer et al. 1992) and Raman spectroscopy (Salje et al. 1993) measurements. Diffuse scattering intensity oriented in planes normal to $[100]$ disappears close to $T_i$ (Kek et al. 1997) and phonon bands associated with TiO₆ octahedral stretching modes exhibit strong softening at $T_i$ (Zhang et al. 1997). Changes in the average crystal structure at $T_i$ amount to small variations in the interatomic distances and angles (mainly reorientation of the Ca displacement vector and slight tilting of the TiO₆ octahedra; Zhang et al. 1997; Malcherek et al. 1999). The occurrence of non-classical effective critical exponents has been reported by a number of authors. Values of $\beta$ have been given as 0.32 (Ghose et al. 1991) and close to 0.15 (e.g., Bismayer et al. 1992; Salje et al. 1993; Chrosch et al. 1997). More recently, Malcherek et al. (2000) and Hayward et al. (2000) both described the phase transition as tricritical, implying a classical value $\beta = 0.25$. Van Heurck et al. (1991) observed antiphase domains in the low temperature phase, with broad and mobile interfaces at and above $T_c$. When the temperature is further increased these antiphase domains disappear. Groat et al. (1996) found that similar behavior does not occur in malayaite, CaSnO₃SiO₄. Most probably, the transition in malayaite is similar to the isosymmetric transition at $T_i$ in titanite. Robbins (1968) was the first to synthesize CaTiOGeO₄. X-ray precession photographs were indexed in $P2_1/n$ with $a = 6.65$, $b = 8.92$, and $c = 7.49$ Å, and $\beta = 119.45$. The present study reports displacive phase transitions in CaTiOGeO₄ and the solid solution it forms with titanite.

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