Evidence for monazite-, barite-, and AgMnO₄ (distorted barite)-type structures of CaSO₄ at high pressure and temperature

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ABSTRACT

Using laser-heated diamond-anvil cells, we have observed CaSO₄ undergoing phase transitions from its ambient anhydrite structure to the monazite type, and at highest pressure and temperature to crystallize in the barite-type structure. On cooling, the barite structure distorts from an orthorhombic to a monoclinic lattice to produce the AgMnO₄-type structure. The barite-structured form of CaSO₄ that we encounter at high pressure and temperature has been, in particular, long expected as a high-pressure phase of CaSO₄-anhydrite from systematic trends of similar A²⁺B⁶⁺O₄-type sulfates, selenates, and tellurates, but has not been observed before. Similarly, the monoclinic distortion of the barite structure itself has been proposed as an intermediate phase between anhydrite and barite types through comparison with the phase diagrams of NaBF₄ and NaClO₄. This result has important consequences for identifying structural trends between different ABO₄-type phases of Group II sulfates, selenates, tellurates, chromates, molybdates and tungstates that crystallize in anhydrite, zircon, monazite, barite and scheelite-type structures at ambient and high pressures.

INTRODUCTION

Since the pioneering experimental work in the 1960s and 1970s that extended the phase diagrams of the A²⁺B⁶⁺O₄ sulfates, selenates, molybdates, and tungstates to pressures (P) up to 12 GPa and temperatures (T) up to ~1000 °C, there has been considerable evidence for systematic trends in phase transitions in ABO₄ isotypes, based on relative cation size (Seifert 1968; Fukugama and Yamaoka 1979; Pannetier and Courtine 1966; Bastide 1987) and similarities with other cationic systems (Pistorius et al. 1969; Muller and Roy 1973; Liu and Bassett 1986). While these trends are now mostly well-established for binary oxides of A²⁺, B⁶⁺, S²⁻, Se²⁻, Te²⁻, stoichiometry, the situation with CaBO₄ (B = S, Se, Te) is intriguing. The stoichiometry CaSO₄ commonly crystallizes in hydrous and anhydrous forms as, respectively, gypsum and anhydrite. The structure adopted by anhydrite is not shared by any other of the A²⁺B⁶⁺O₄ chemistries; it does exist as both ammonium and potassium perchlorate (Gottfried and Schusterius 1932). Therefore its place, as an exception in the systematic, is of importance in establishing the trends of high P phase transitions between the “lower-P” (smaller cation) sulfates and chromates of Cr₂O₃ and zircon-types [e.g., MgSO₄, MgCrO₄, CaCrO₄ (chromatite); Rentzeperis and Soldatos 1958; Muller et al. 1969; Clouse 1932] and the anticipated “moderate-P” (larger cation) forms of sulfates and chromates that crystallize with monazite-and barite-type structures (e.g., SrCrO₄, BaSO₄, SrMoO₄; Pistorius and Pistorius 1962; Jacobson et al. 1998). If we extend this further, a link can then be constructed toward the “high-P” structures of the selenates, molybdates, and tungstates that form primarily primarily with barite- and scheelite-type structures (e.g., SrSeO₄, BaSeO₄, RaSeO₄, SrMoO₄, BaMoO₄, RaMoO₄, CaMoO₄, CaWO₄, BaWO₄, and RaWO₄; Pistorius and Pistorius 1962; Egorov-Tismenko et al. 1967; Guermen et al. 1971). It is therefore evident that understanding the high-P phase transformations of CaSO₄ in the broader framework of structural systematics is the key to successful anticipation of true high-P forms.

Given the relationships outlined above, it comes as little surprise that much effort has been made to identify post-anhydrite forms of CaSO₄, with the principle aim being to find the structural modification of CaSO₄ crystallizing with the barite structure. This has met with encouraging results (e.g., Borg and Smith 1975) in that the denser monazite (CePO₄)-form of CaSO₄ has been identified as the next high-P phase. This result confirmed that the larger-cation-hosting SrSeO₄ and SrCrO₄ (both monazites) are good model structures for the smaller cation CaSO₄ phase under high pressure. Nonetheless, observation of the barite variant, and its distorted AgMnO₄ precursor, which was also predicted by Pistorius et al. (1969) as a post-anhydrite phase, have remained elusive with the most recent study recovering an as yet unidentified ex situ orthorhombic structure from in situ high-P laser-heated Raman experiments (Chen et al. 2001). Although the barite phase was not found, Chen et al. (2001) did positively identify, through continuous observation of the ν₄-SO₄ Raman bands, that the [SO₄]²⁻ structural unit did remain intact over their entire P-T range, thus limiting the possible structures at high P (and T) to those with fourfold coordinated B cations. Nevertheless, there has been some doubt about the true sequence of the post-anhydrite phases of CaSO₄; scheelite (CaWO₄-type, adopted by CaSeO₄; e.g., JCPDS card 36-0932), CaSeO₄ [shown to also crystallize from the dihydrate in P2₁a₂, Snyman and Pistorius (1963), though these authors consider the possibility that the structure is that of crocoite (PbCrO₄), i.e., monazite-