

Thermal behavior of polyhalite: a high-temperature synchrotron XRD study

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Abstract As an accessory mineral in marine evaporites, polyhalite, $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$, coexists with halite (NaCl) in salt formations, which have been considered as potential repositories for permanent storage of high-level nuclear wastes. However, because of the heat generated by radioactive decays in the wastes, polyhalite may dehydrate, and the released water will dissolve its neighboring salt, potentially affecting the repository integrity. Thus, studying the thermal behavior of polyhalite is important. In this work, a polyhalite sample containing a small amount of halite was collected from the Salado formation at the WIPP site in Carlsbad, New Mexico. To determine its thermal behavior, in situ high-temperature synchrotron X-ray diffraction was conducted from room temperature to 1066 K with the sample powders sealed in a silica-glass capillary. At about 506 K, polyhalite started to decompose into water vapor, anhydrite ($CaSO_4$) and two langbeinite-type phases, $K_2Ca_xMg_{2-x}(SO_4)_3$, with different Ca/Mg ratios. XRD peaks of the minor halite disappeared, presumably due to its dissolution by water vapor. With further increasing temperature, the two langbeinite solid solution phases displayed complex variations in crystallinity, composition and their molar ratio and then were combined into the single-phase triple salt, $K_2CaMg(SO_4)_3$, at ~919 K. Rietveld analyses of the XRD data allowed determination of structural parameters of polyhalite and its decomposed anhydrite and langbeinite phases as a function of temperature. From the

results, the thermal expansion coefficients of these phases have been derived, and the structural mechanisms of their thermal behavior been discussed.

Keywords Polyhalite · Thermal decomposition · Anhydrite · Langbeinite · Crystal structure · Thermal expansion · Synchrotron X-ray diffraction · Salt repository

Introduction

Polyhalite, $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$, coexists with halite and anhydrite in marine evaporites. Though not a major mineral, it occurs widely in evaporites, especially rock salt formations (Stewart 1963). Polyhalite has also been reported to occur in atmospheric particles, which may interact with incoming solar radiation and thus affect the climate and weather (Jentzsch et al. 2012). Commercially, polyhalite is mined as a potassium source. In addition, polyhalite is used as an organic fertilizer (Barbarick 1991) or a raw material for the production of specialty fertilizers, because it contains four important nutrient elements (K, Mg, Ca and S) for crop growth while being low in chlorine.

Most interests in polyhalite with geological relevance have been on its occurrence in rock salt formations, which can serve as geological repositories for disposal of nuclear wastes. For example, the Waste Isolation Pilot Plant (WIPP), located in Carlsbad, New Mexico, is a salt repository used for storing transuranic radioactive waste from nuclear weapon activities. More recently, salt repositories have been considered as an attractive option for immobilization of heat-generating used nuclear fuel (UNF) and high-level waste (HLW), as salt has several advantageous attributes, including impermeability, self-sealing (plasticity) and good thermal conductivity, at repository conditions (Hansen and Leigh

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2011). However, since salt formations contain halite crystals with brine inclusions and small amounts of hydrous minerals such as polyhalite, gypsum and clay (Nathans 1963; Weck et al. 2014), one must consider the thermal behavior of these water-bearing phases, when UNF/HLW radionuclides release heat upon decays to daughter elements. Polyhalite is an important hydrous mineral coexisting with halite, and to evaluate the suitability of salt repositories for UNF/HLW disposal, its thermal behavior needs to be studied.

Polyhalite and its analogues (Wollmann et al. 2008, 2009) crystallize in a triclinic symmetry with the space group $F\bar{1}$ (Schlatti et al. 1970) or $P\bar{1}$ (Bindi 2005). The structure consists of $[\text{SO}_4]$ tetrahedra, $[\text{MgO}_6]$ octahedra and $[\text{CaO}_8]$ triangular dodecahedra with K situating in an 11-oxygen-coordinated position (Fig. 1a). Each H_2O oxygen is bonded to one Mg^{2+} and one K^+ . Previous studies show that polyhalite is stable up to a temperature ranging from 508 to 578 K in a “dry” environment (The temperature ranges are different in the brine-containing K–Ca–Mg–Na–Cl– SO_4 – H_2O system; Kropp and Holldorf 1988; Kropp et al. 1988), at which it starts to undergo dehydration (Fischer et al. 1996 and references therein). The relatively large range of dehydration temperatures is likely due to differences in experimental conditions (e.g., partial water vapor pressure, heating rate and the flowing gas used) and sample characteristics (e.g., crystallinity) (Nathans 1963). Moreover, concomitant with the dehydration of polyhalite is its decomposition into anhydrite (insoluble, β - CaSO_4) and triple salt $\text{K}_2\text{CaMg}(\text{SO}_4)_3$, the latter of which decomposes further into two solid solution phases, $\text{K}_2\text{Ca}_{0.24}\text{Mg}_{1.76}(\text{SO}_4)_3$ and $\text{K}_2\text{Ca}_{1.36}\text{Mg}_{0.64}(\text{SO}_4)_3$ (Fischer et al. 1996). Note that the above results were mostly obtained using differential scanning calorimetry (DSC) and thermogravimetry (TG) for reaction heat and weight loss analysis, and X-ray diffraction (XRD) for identification of quenched, decomposed phases. However, as for any ex situ measurements, there is always a question regarding whether the quenched samples for XRD represent the phases at high temperatures. In addition, structural evolution of these phases (except for anhydrite) with temperature and underlying mechanisms for the decomposition reactions are not well known.

To examine the thermal decomposition of polyhalite in situ and to determine the structural parameters of associated phases at elevated temperatures, we perform high-temperature synchrotron XRD experiments up to 1066 K. At about 506 K, polyhalite started to decompose into water vapor, anhydrite and two langbeinite solid solution phases along the $\text{K}_2\text{SO}_4 \cdot 2 \text{MgSO}_4 - \text{K}_2\text{SO}_4 \cdot 2 \text{CaSO}_4$ join. On further heating to ~919 K, the two langbeinite phases changed their Ca/Mg ratios and relative amounts and were eventually combined into the single-phase triple salt, $\text{K}_2\text{CaMg}(\text{SO}_4)_3$. Rietveld analyses of the XRD data allowed the determination of structural parameters of polyhalite and its

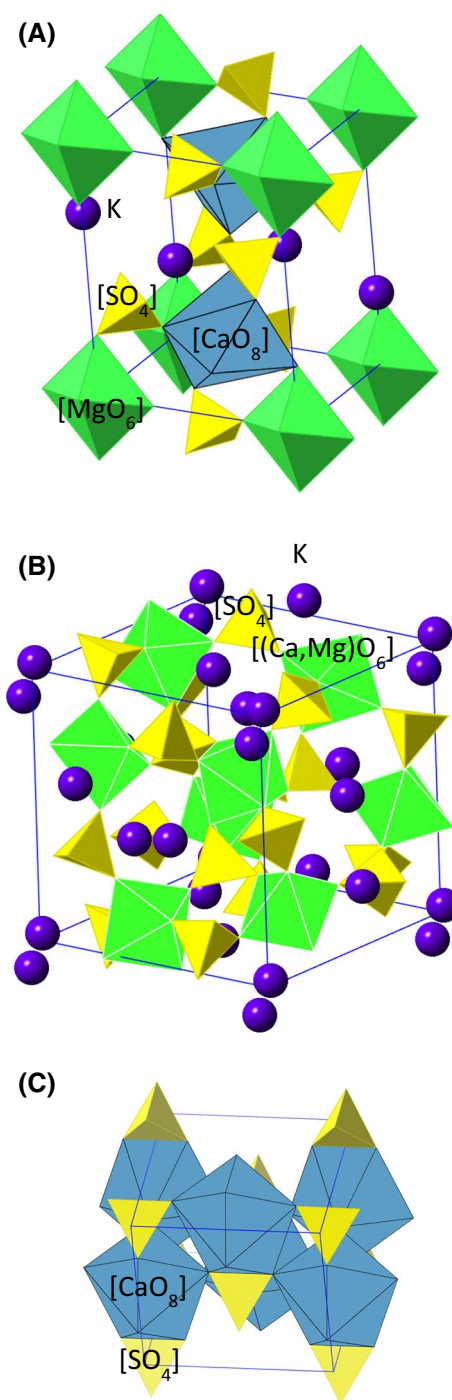


Fig. 1 Crystal structures of **a** polyhalite, $\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$; **b** langbeinite, $\text{K}_2(\text{Ca,Mg})_2(\text{SO}_4)_3$ and **c** anhydrite CaSO_4 . Tetrahedra represent $[\text{SO}_4]$ units, octahedra represent $[\text{MgO}_6]$ or $[(\text{Ca,Mg})\text{O}_6]$ units, eight-vertex polyhedra represent $[\text{CaO}_8]$ units, and spheres represent K^+ cations

decomposed anhydrite and langbeinite phases as a function of temperature. From these results, the coefficients of thermal expansion (CTEs) have been determined and the related structural mechanisms been discussed.

Experimental methods

Sample

A polyhalite sample containing a small amount of halite was collected from the Salado formation at the WIPP site. The Salado formation is part of the late Permian Ochoan series in western Texas and southeastern New Mexico, and consists of flat-lying beds, which are composed of dominantly halite coexisting with other minor minerals including anhydrite, polyhalite, dolomite and clay (Lowenstein 1988). The polyhalite sample appears as fine-grained masses with a reddish color, presumably because of the presence of thin iron oxide coatings on polyhalite grains.

The composition and homogeneity of the sample were analyzed using a Cameca SX100 electron microprobe operated at an accelerating voltage of 15 keV and a beam current of 20 nA. Wavelength dispersive spectroscopy was used to determine the amounts of K, Mg and Ca with KAlSi_3O_8 (orthoclase), MgO and CaSO_4 as the standards, respectively. The determined K/Ca/Mg ratio is 1.97:1.92:1, close to the ideal stoichiometry of 2:2:1. In addition, back-scattered electron imaging showed that the sample is homogenous at least at the micron scales.

Thermal analysis

To determine the water content of the polyhalite sample, and also to examine its thermal behavior, TG and DSC measurements were conducted using a Netzsch simultaneous thermal analyzer (STA) 449 system. About 15 mg of the sample powders was packed in a standardized Pt crucible. The loaded crucible was then placed into the calorimeter and heated to 1173 K with a rate of 10 K/min under an Ar atmosphere. For baseline correction, an earlier scan using the empty Pt crucible was run under the same conditions. Temperature was calibrated against the melting points of several metal standards (e.g., In and Al), and sensitivity calibration was done using the heat capacities of sapphire.

In situ powder synchrotron X-ray diffraction and Rietveld analysis

In situ high-temperature powder XRD measurements were carried out at beam line X14A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) (Chung et al. 2000). The wavelength used was 0.7748821 Å, as calibrated using a NIST SRM 660a LaB_6 standard. Sample powders were sealed in a silica-glass capillary of 0.7 mm diameter, and data were collected at 22 temperature points ranging from 303 to 1066 K with a position-sensitive silicon strip detector. Each data scan was run over a 2θ range from 3° to 56° for about 13 min except

the data at 553 K, which was held for about one hour due to unavailability of synchrotron X-rays. The combined use of intense synchrotron beam, capillary configuration and fast Si-strip detector was ideal for achieving high angular resolution and high-speed data collection for in situ XRD measurements.

The obtained synchrotron XRD data were analyzed by the Rietveld method with the General Structure Analysis System (GSAS) program of Larson and Von Dreele (2000). The starting parameters for the refinement at 303 K were taken from the study of polyhalite at room temperature by Bindi (2005). Since the sample contains a small amount of NaCl, we refined the weight fractions of polyhalite and halite with the constraint that the individual weight fractions sum to unity. We then used the results as the starting structure for the next nearest temperature and continued this procedure systematically with increasing temperature. Similar procedures were used for structural refinements of the decomposed anhydrite and langbeinite phases and determination of their molar ratios at higher temperatures. The starting structural parameters for the anhydrite and langbeinite refinements (Fig. 1b, c) were taken from the studies by Morikawa et al. (1975) and Pekov et al. (2012), respectively. Our refinements generally proceeded as follows: After the scale factor and four background terms (shifted Chebyshev function) had converged, specimen displacement and lattice parameters were added and optimized. Sixteen additional background terms were then added, and the peak profiles were fitted to pseudo-Voigt convolution functions with a peak asymmetry correction (Thompson et al. 1987; Finger et al. 1994). On convergence of the preceding parameters, the atomic coordinates and atomic isotropic temperature factors of K, Ca, Mg, S and O were refined (The temperature factors of like atoms are constrained to be equal). The final refinements yielded R_{wp} values ranging from 3.30 to 5.51 % and R_p from 2.54 to 3.75 % (Tables 1, 2). A representative fitted pattern is plotted in Fig. 2. The refined unit-cell parameters are listed in Tables 1 and 2, and the atomic positions and displacement parameters of polyhalite, anhydrite and langbeinite at selected temperatures (303 K for polyhalite, 648 K for anhydrite and 1023 K for langbeinite) are listed in Tables 3, 4 and 5, respectively.

Results and discussion

Thermal analysis

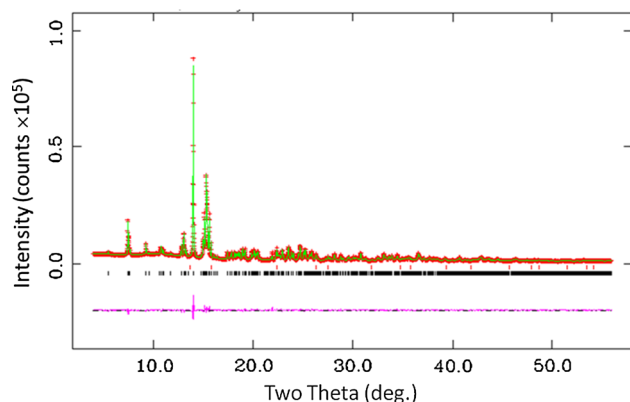
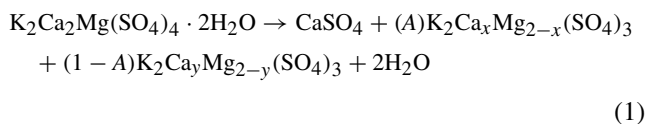
Figure 3 shows the TG/DSC curves obtained by heating the polyhalite sample to 1173 K. As is shown, there is an endothermic DSC peak at 616.4 K, which corresponds to a weight loss of 5.80 %. These are due to the following reaction, as revealed by in situ high-temperature synchrotron XRD (see below):

Table 1 Unit-cell parameters and refinement agreement indices of polyhalite

T (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)	<i>R</i> _{wp} (%)	<i>R</i> _p (%)
303	6.96032(9)	6.95826(9)	8.8961(1)	104.070(1)	101.223(1)	113.900(1)	360.616(8)	4.17	3.15
319	6.96042(9)	6.95836(9)	8.8965(1)	104.071(1)	101.224(1)	113.898(1)	360.643(9)	4.21	3.18
334	6.9615(1)	6.95970(9)	8.9046(1)	104.085(1)	101.235(1)	113.849(1)	361.215(9)	4.32	3.27
396	6.9642(1)	6.96547(9)	8.9340(1)	104.125(1)	101.285(1)	113.653(1)	363.336(9)	4.12	3.18
443	6.9660(1)	6.9696(1)	8.9546(1)	104.157(1)	101.326(1)	113.513(1)	364.81(1)	4.16	3.17
490	6.9667(1)	6.9723(1)	8.9760(1)	104.199(1)	101.368(1)	113.351(1)	366.23(1)	4.33	3.26

Table 2 Unit-cell parameters and refinement agreement indices of anhydrite and langbeinite phases

T (K)	<i>a</i> _{anh} (Å)	<i>b</i> _{anh} (Å)	<i>c</i> _{anh} (Å)	<i>V</i> _{anh} (Å ³)	<i>a</i> _{lan-Ca} (Å)	<i>V</i> _{lan-Ca} (Å ³)	<i>a</i> _{lan-Mg} (Å)	<i>V</i> _{lan-Mg} (Å ³)	<i>R</i> _{wp} (%)	<i>R</i> _p (%)
553	7.0226(2)	7.0195(2)	6.3073(1)	310.92(2)	10.2665(3)	1082.10(9)	10.135(1)	1041.0(3)	3.30	2.54
585	7.0256(2)	7.0209(2)	6.3147(1)	311.48(2)	10.2732(3)	1084.22(9)	10.136(3)	1041.3(8)	3.53	2.68
600	7.0273(2)	7.0210(2)	6.3175(1)	311.70(2)	10.2761(2)	1085.13(7)	10.127(2)	1038.6(7)	3.39	2.61
632	7.0317(1)	7.0234(1)	6.32437(8)	312.34(1)	10.2847(2)	1087.85(6)	10.120(1)	1036.3(4)	3.55	2.71
648	7.03276(9)	7.02381(9)	6.32712(7)	312.539(9)	10.2884(2)	1089.04(6)	10.1016(8)	1030.8(2)	3.64	2.74
679	7.0355(1)	7.0250(1)	6.33369(8)	313.04(1)	10.3158(2)	1097.76(7)	10.120(1)	1036.6(3)	5.51	3.75
725	7.03992(5)	7.02690(5)	6.34246(4)	313.754(5)	10.32531(8)	1100.80(2)	10.0867(2)	1026.23(6)	3.62	2.72
770	7.04346(4)	7.02808(4)	6.35287(3)	314.480(4)	10.32676(6)	1101.27(2)	10.0988(2)	1029.94(5)	3.43	2.59
815	7.04890(4)	7.03123(4)	6.36315(3)	315.373(4)	10.32819(7)	1101.72(2)	10.1106(2)	1033.56(5)	3.64	2.66
860	7.05172(4)	7.03220(4)	6.37129(3)	315.947(4)	10.30955(7)	1095.77(2)	10.1207(2)	1036.66(5)	3.52	2.57
919	7.05687(4)	7.03387(4)	6.38421(3)	316.893(5)	10.28371(8)	1087.55(3)	–	–	4.18	2.87
964	7.06039(4)	7.03547(4)	6.39630(3)	317.724(5)	10.28685(8)	1088.55(2)	–	–	4.09	2.71
1023	7.06606(4)	7.03682(4)	6.41176(3)	318.810(4)	10.31506(5)	1097.53(2)	–	–	3.70	2.61
1066	7.06906(6)	7.03671(6)	6.42142(5)	319.420(7)	10.3541(5)	1110.0(2)	–	–	5.47	3.02

**Fig. 2** Fitted synchrotron XRD pattern of polyhalite at 303 K. Data are shown as plus signs, and the solid curve is the best fit to the data. Tick marks below the pattern show the positions of allowed reflections, and the lower curve represents the difference between the observed and calculated profiles

where polyhalite dehydrates into anhydrite, two langbeinite-type phases with different Ca/Mg ratios and water vapor (*A* and *1–A* are the numbers of moles of the two langbeinite phases). Although the DSC peak is at 616.4 K, the dehydration process occurs over the temperature range ~510–660 K. Thus, the onset temperature of dehydration (~510 K) lies within the reported range of 508–578 K (Fischer et al. 1996) (though at the lower end). The weight loss of 5.80 % is slightly lower than that (5.98 %) corresponding to the ideal polyhalite composition $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, presumably due to the presence of a small amount of NaCl in the sample. At 1143.7 K, there is another large, yet sharper endothermic peak with no corresponding weight loss. This is likely due to the melting of langbeinite solid solutions based on the ternary K_2SO_4 – MgSO_4 – CaSO_4 phase diagram (Rowe et al. 1967).

High-temperature synchrotron XRD

Figure 4a, b plots the XRD patterns in the temperature range from 303 K to 1066 K. With increasing temperature, polyhalite remained stable up to 490 K (Fig. 4a). However, when the temperature reached 506 K, it started

Table 3 Atomic coordinates and atomic thermal parameters of polyhalite at 303 K (space group $P\bar{1}$)

Atom	x	y	z	U_{iso} ($\text{\AA}^2/100$)
Mg	0	0	0	2.2(1)
Ca	0.1254(3)	0.3655(4)	−0.2588(2)	0.16(5)
K	0.5253(3)	0.7880(3)	0.5736(2)	1.25(7)
S(1)	0.3160(4)	0.5649(4)	0.1412(3)	1.14(5)
S(2)	−0.0583(4)	0.1885(4)	0.3570(3)	1.14(5)
O(1)	−0.0337(8)	0.0097(8)	0.2391(5)	0.92(5)
O(2)	0.1249(8)	0.3353(7)	0.0405(6)	0.92(5)
O(3)	0.5032(7)	0.5564(8)	0.2423(6)	0.92(5)
O(4)	−0.2270(7)	0.3152(7)	0.7581(5)	0.92(5)
O(5)	0.3855(7)	0.6860(8)	0.0268(6)	0.92(5)
O(6)	−0.1794(7)	0.2773(7)	0.2669(6)	0.92(5)
O(7)	−0.1824(8)	0.0811(8)	0.4530(6)	0.92(5)
O(8)	0.1675(8)	0.3539(8)	0.4662(5)	0.92(5)
O(9)	0.3151(7)	0.0441(9)	0.0793(6)	0.92(5)

Table 4 Atomic coordinates and atomic thermal parameters of anhydrite at 648 K (space group $Bmmb$)

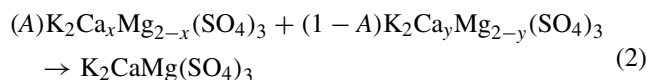
Atom	x	y	z	U_{iso} ($\text{\AA}^2/100$)
Ca	0	0.25	0.3434(5)	1.32(8)
S	0	0.75	0.1581(7)	1.7(1)
O(1)	0.1725(6)	0.75	0.0264(5)	2.5(1)
O(2)	0	0.5829(6)	0.3010(7)	2.5(1)

Table 5 Atomic coordinates and atomic thermal parameters of langbeinite, $K_2CaMg(SO_4)_3$, at 1023 K (space group $P2_13$)

Atom	x	y	z	U_{iso} ($\text{\AA}^2/100$)
K(1)	0.8145(6)	0.8145(6)	0.8145(6)	8.6(2)
K(2)	0.0518(4)	0.0518(4)	0.0518(4)	8.6(2)
Ca/Mg(1)	0.3278(4)	0.3278(4)	0.3278(4)	3.0(1)
Ca/Mg(2)	0.5946(4)	0.5946(4)	0.5946(4)	3.0(1)
S	0.2216(4)	0.3757(9)	0.0110(7)	4.3(1)
O(1)	0.302(1)	0.277(2)	0.958(1)	8.9(2)
O(2)	0.093(1)	0.328(1)	0.013(1)	8.9(2)
O(3)	0.230(1)	0.483(2)	0.922(2)	8.9(2)
O(4)	0.269(1)	0.409(1)	0.134(2)	8.9(2)

to decompose into anhydrite, two langbeinite phases and water vapor. Thus, the onset temperature of this decomposition is between 490 and 506 K, which is lower than that (510 K) from the TG/DSC measurements. This difference is likely due to kinetic factors; for the TG/DSC measurements, the temperature was increased continuously with a rate of 10 K/min, whereas in the XRD experiments, the

temperature was increased stepwise with a dwell time of ~13 min–1 h at each temperature. The longer annealing time used in the XRD experiments facilitated the polyhalite decomposition reaction, resulting in a lower onset temperature. When the temperature was increased to 600 K, no diffraction peaks from polyhalite were discerned, suggesting completion of the polyhalite decomposition (Fig. 4a). On further heating to 919 K, the two langbeinite phases were combined into a single-phase triple salt, $K_2CaMg(SO_4)_3$, as follows (Fig. 4a):



This reaction was not evident in the DSC curve (Fig. 3), presumably due to the small heat effect involved. It should be also noted that, upon polyhalite dehydration, we did not detect the $K_2CaMg(SO_4)_3$ triple salt prior to the formation of the two langbeinite phases, as hypothesized by Fischer et al. (1996). Rather, the triple salt was a product of combination of the two langbeinite phases at higher temperatures. This behavior is consistent with the increased tolerance of accommodating different sizes of ions (Ca^{2+} and Mg^{2+} herein) in a crystal structure with increasing temperature, thereby resulting in increased solubility limit of the solid solution (Putnis 1992).

Thermal expansion of polyhalite

Rietveld analysis of the synchrotron XRD data of polyhalite (Fig. 2) in the temperature range from 303 to 490 K allowed determination of its structural parameters as a function of temperature. The room-temperature parameters are consistent with those from previous studies (e.g., Bindi 2005; Weck et al. 2014), and the high-temperature values are reported for the first time. Figure 5 shows temperature dependence of unit-cell parameters a , b , c (Fig. 5a), α , β , γ (Fig. 5b) and V (Fig. 5c). Fitting the data to linear relations yielded:

$$a = 3.8790 \times 10^{-5}T + 6.9486 \quad R^2 = 0.980 \quad (3)$$

$$b = 7.9461 \times 10^{-5}T + 6.9336 \quad R^2 = 0.990 \quad (4)$$

$$c = 4.423 \times 10^{-4}T + 8.7584 \quad R^2 = 0.995 \quad (5)$$

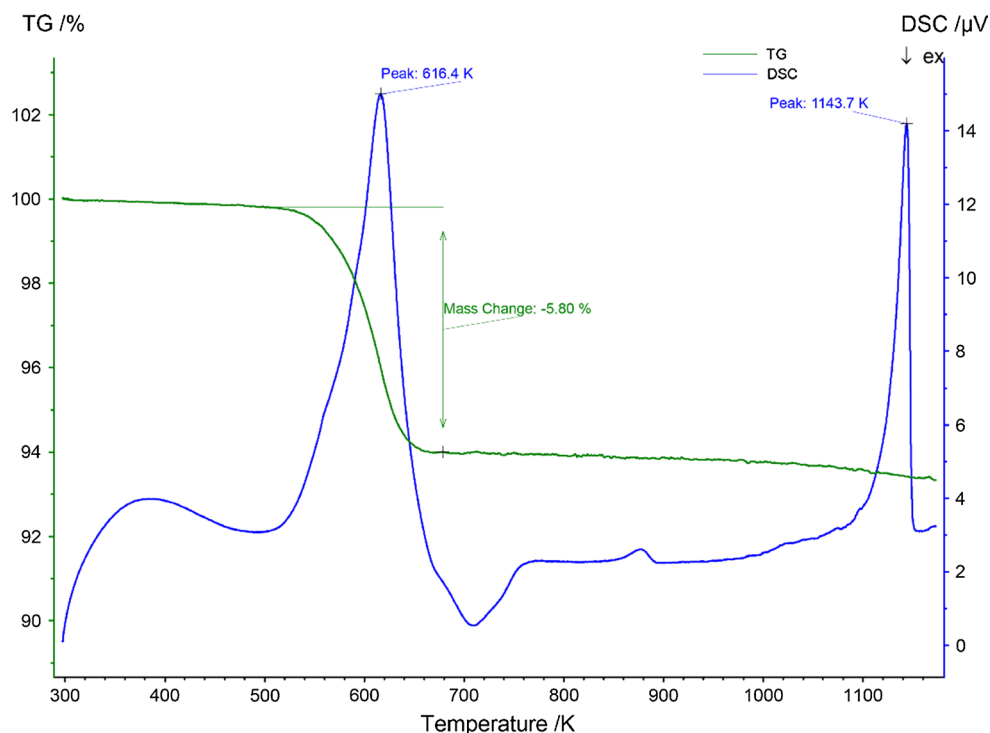
$$\alpha = 6.859 \times 10^{-4}T + 103.8555 \quad R^2 = 0.992 \quad (6)$$

$$\beta = 8.111 \times 10^{-4}T + 100.9694 \quad R^2 = 0.993 \quad (7)$$

$$\gamma = -3.037 \times 10^{-3}T + 114.8503 \quad R^2 = 0.994 \quad (8)$$

$$V = 3.14 \times 10^{-2}T + 350.85 \quad R^2 = 0.995 \quad (9)$$

Fig. 3 TG and DSC curves of polyhalite from room temperature to 1173 K



from which the CTEs of polyhalite are derived as follows: $\alpha_a = 5.572 \times 10^{-6} \text{ K}^{-1}$; $\alpha_b = 1.142 \times 10^{-5} \text{ K}^{-1}$; $\alpha_c = 4.970 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_V = 8.701 \times 10^{-5} \text{ K}^{-1}$. Hence, the thermal expansion of polyhalite is highly anisotropic; the ratios of its axial CTEs $\alpha_a/\alpha_b/\alpha_c = 1:2.05:8.92$. The larger α_c compared with α_a and α_b may be attributed to the layered nature of the polyhalite structure. As shown in Fig. 5d, the structure may be considered to consist of interpenetrating layers of $[\text{KO}_{11}]$, $[\text{CaO}_8]$, $[\text{MgO}_6]$ and $[\text{SO}_4]$ polyhedra parallel to (001). Since the forces between the layers are weaker than those within the layers, the **c**-axis exhibits a much larger CTE than those along **a** and **b** axes. With regard to α_a and α_b , α_b is about 2 times α_a . This can be explained in terms of local bonding environments of neighboring $[\text{KO}_{11}]$ polyhedra (Fig. 5e). Because $[\text{KO}_{11}]$ polyhedra are linked via face-sharing to form chains along [010], the **b**-axis expands more rapidly than **a** to minimize repulsion between neighboring K^+ cations, resulting in a larger α_b compared with α_a .

Thermal expansion of anhydrite

Since the polyhalite sample decomposed into anhydrite and langbeinite phases at high temperatures, we obtained structural parameters of these decomposed phases as a function of temperature from Rietveld analysis. Figure 6 plots temperature dependence of unit-cell parameters *a*, *b*, *c* (Fig. 6a) and *V* (Fig. 6b) of anhydrite (insoluble, β - CaSO_4 ; there is another polymorph of CaSO_4 , which is soluble and named as γ -anhydrite). Fitting the data to linear relations yielded:

$$a = 8.9120 \times 10^{-5}T + 6.9746 \quad R^2 = 0.997 \quad (10)$$

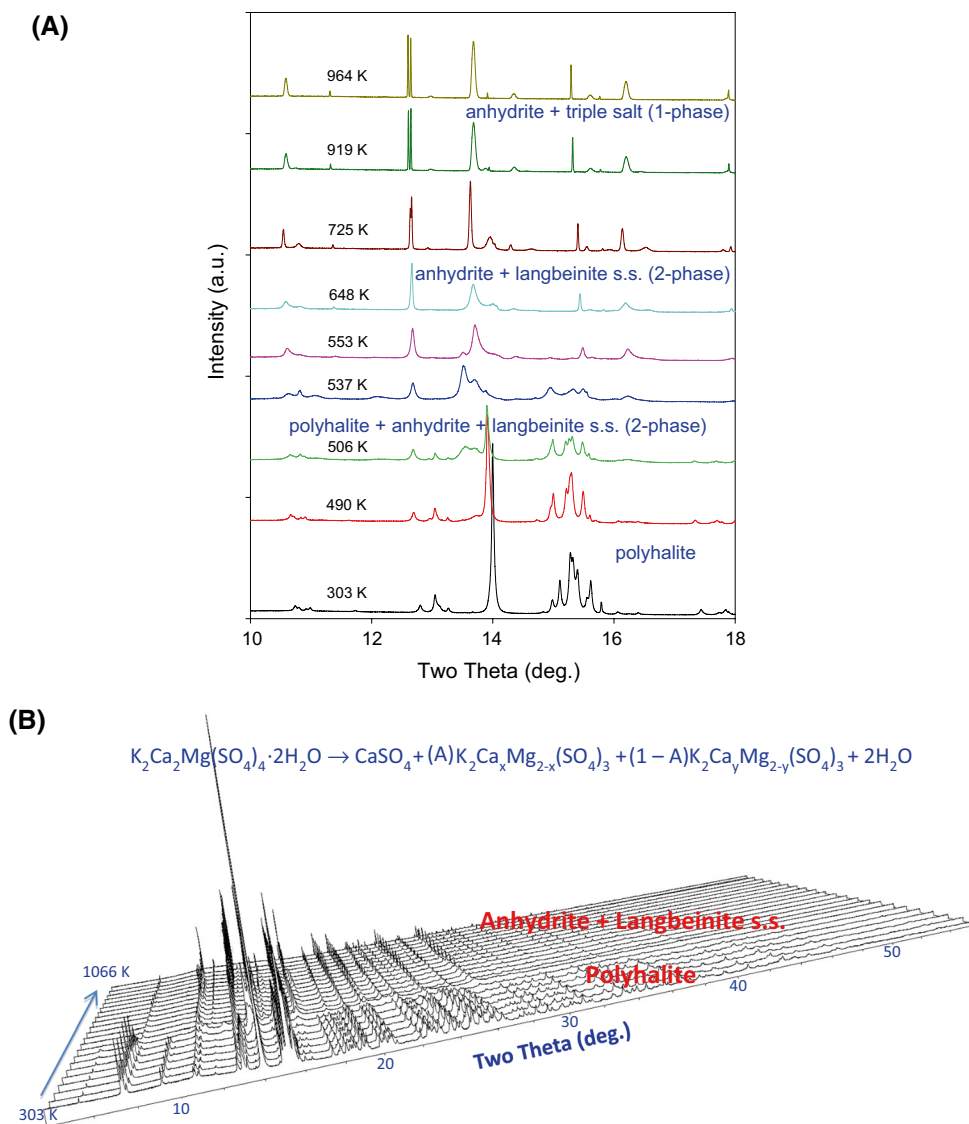
$$b = 3.4316 \times 10^{-5}T + 7.0015 \quad R^2 = 0.973 \quad (11)$$

$$c = 2.210 \times 10^{-4}T + 6.1839 \quad R^2 = 0.998 \quad (12)$$

$$V = 1.647 \times 10^{-2}T + 301.8451 \quad R^2 = 0.9995 \quad (13)$$

from which the CTEs of anhydrite are derived as follows: $\alpha_a = 1.269 \times 10^{-5} \text{ K}^{-1}$; $\alpha_b = 4.888 \times 10^{-6} \text{ K}^{-1}$; $\alpha_c = 3.505 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_V = 8.297 \times 10^{-5} \text{ K}^{-1}$. These results are in agreement with those of Ballirano and Melis (2007), but less so with those of Evans (1979); the earlier employed higher-resolution parallel-beam laboratory XRD, compared with the Guinier-Lenné technique with limited accuracy used by the latter. As in polyhalite, the unit cell of anhydrite expands anisotropically on heating; its **c**-axis lengthens most significantly. This behavior may be attributed to the expansion of $[\text{CaO}_8]$ polyhedron, whose two longest Ca–O bonds are oblique with low angles to the **c**-axis. As shown in Fig. 6c, the anhydrite structure comprises chains of alternating edge-shared $[\text{SO}_4]$ tetrahedra and $[\text{CaO}_8]$ polyhedra (distorted triangular dodecahedra) along **c** (Hawthorne and Ferguson 1975). As the temperature increases, while $[\text{SO}_4]$ tetrahedron remains largely unchanged, $[\text{CaO}_8]$ polyhedron expands more pronouncedly along the $[\text{SO}_4]/[\text{CaO}_8]$ chain parallel to **c** to minimize the repulsion between neighboring S^{6+} and Ca^{2+} , thereby resulting in a larger α_c .

Fig. 4 Synchrotron XRD patterns from 303 to 1066 K. **a** Selected patterns; **b** 3-D plot of all the patterns



Thermal behavior of langbeinite solid solutions

As stated earlier, polyhalite starts to dehydrate into two langbeinite-type phases, $\text{K}_2\text{Ca}_x\text{Mg}_{2-x}(\text{SO}_4)_3$, with different x values, plus anhydrite at ~ 506 K. The two langbeinite phases display complex variations in crystallinity, composition and molar ratio with increasing temperature. Note that in the langbeinite structure, Ca and Mg occupy the same octahedral site, forming the $\text{K}_2(\text{Ca,Mg})_2(\text{SO}_4)_3$ solid solution series along the $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ — $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ join (Morey et al. 1964). At room temperature, the end member $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ adopts an orthorhombic structure (space group $P2_12_12_1$) containing heavily distorted $[\text{CaO}_6]$ octahedra, and it transforms to a cubic phase (space group $P2_13$), whose $[\text{CaO}_6]$ octahedra are less distorted, on heating above 457 K (Speer and Salje 1986). By contrast, the end member $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ adopts the cubic structure up to its melting point (Zemann and Zemann

1957; Mereiter 1979; Speer and Salje 1986), though it transforms to lower-symmetry phases below room temperature (Boerio-Goates et al. 1990). Hence, the $\text{K}_2(\text{Ca,Mg})_2(\text{SO}_4)_3$ solid solutions formed upon polyhalite dehydration (>506 K) possess the same structure of $P2_13$ (Fig. 1b). Figure 7 shows the fitted synchrotron XRD patterns of langbeinite (and the coexisting anhydrite) at 600, 860, 1023 and 1066 K. At 600 K, the crystallinity of the Ca-rich phase was higher than that of the Mg-rich phase, as reflected by the sharper peaks of the earlier (Fig. 7a). On heating to 860 K (Fig. 7b), the overlapped peaks of the two phases became well resolved, due to their increased crystallinity. However, at higher temperatures, e.g., 1023 K (Fig. 7c), the Mg-rich phase disappeared. This behavior suggests a complete combination of the two phases into the triple salt, $\text{K}_2\text{CaMg}(\text{SO}_4)_3$, a member of the $\text{K}_2\text{Ca}_x\text{Mg}_{2-x}(\text{SO}_4)_3$ series with $x = 1$. With further increasing the temperature to 1066 K, the triple salt started

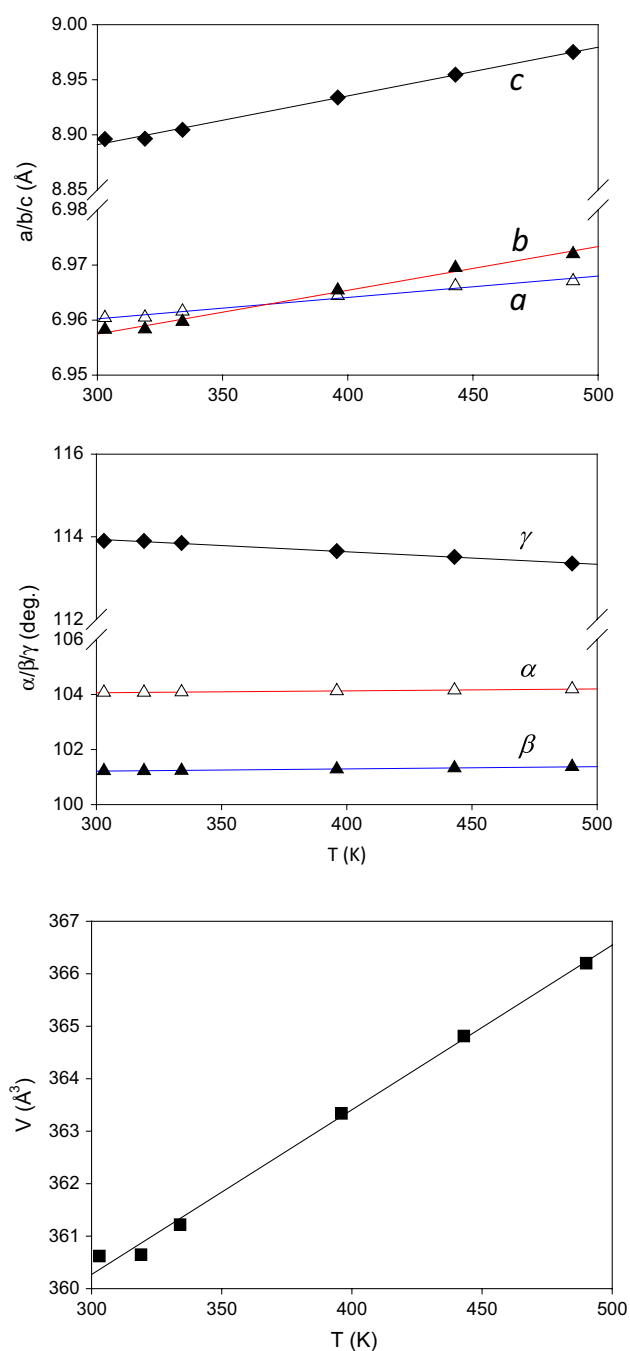
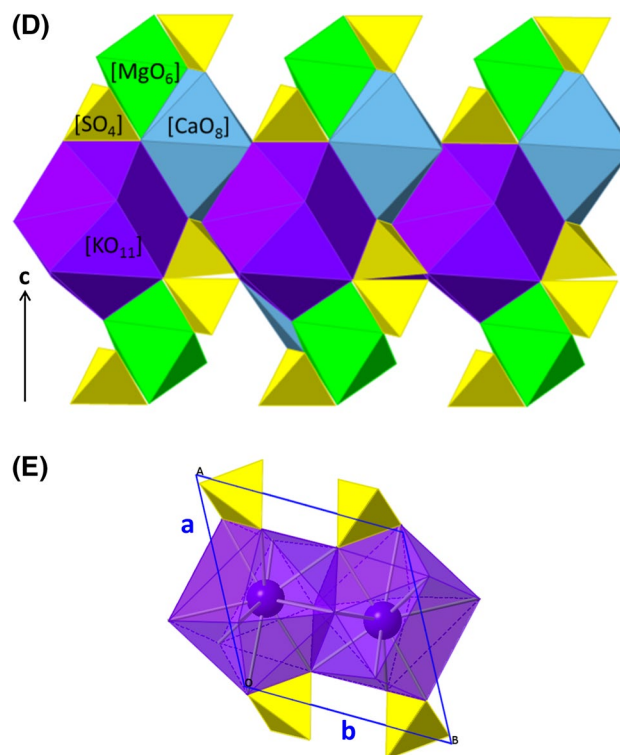


Fig. 5 Variation of unit-cell parameters **a** a , b , c ; **b** α , β , γ and **c** cell volume V of polyhalite as a function of temperature. **d** Projection of the structure of polyhalite down $[\bar{1}\bar{1}0]$. **e** Schematic showing coordi-



nation environments of neighboring K^+ cations in the polyhalite structure

to melt, as evidenced by the disappearance of some of its diffraction peaks, resulting in a poor fit of its entire XRD pattern (Fig. 7d). This melting is also evident in the DSC curve with an endothermic peak in the temperature range of ~1050–1150 K (Fig. 3).

Figure 8 shows variations of unit-cell parameter a (Fig. 8a) of the two langbeinite phases and their molar

ratios (Fig. 8b) as a function of temperature. With increasing temperature to 648 K, the cell parameter a of the Ca-rich phase increased whereas that of the Mg-rich phase decreased. Since thermal expansion would lead to increases in a in both phases, the observed trends in Fig. 8a imply that there must have existed compositional variations with temperature. In particular, the decreases in a in the Mg-rich

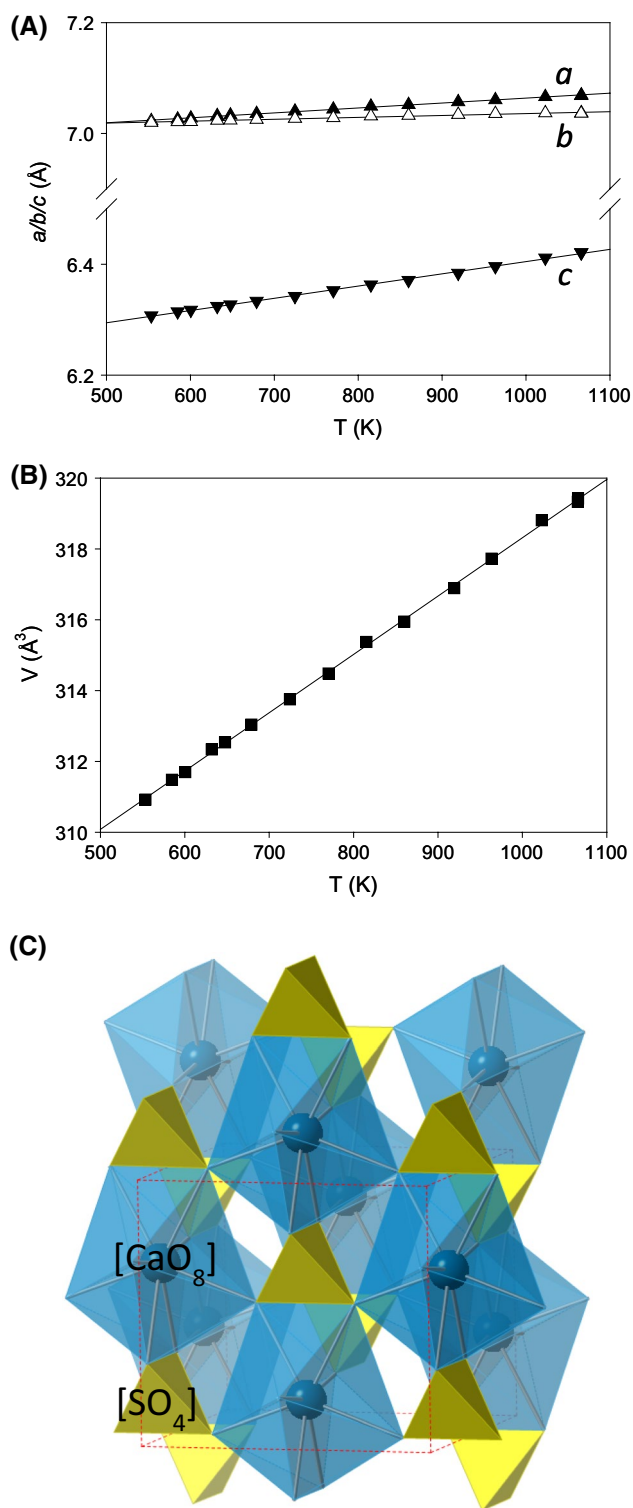


Fig. 6 Variation of unit-cell parameters **a**, **b** and **c** and **b** cell volume V of anhydrite as a function of temperature. **c** Schematic showing chains of alternating edge-sharing $[\text{SO}_4]$ tetrahedra and $[\text{CaO}_8]$ polyhedra along the c -axis of the anhydrite structure

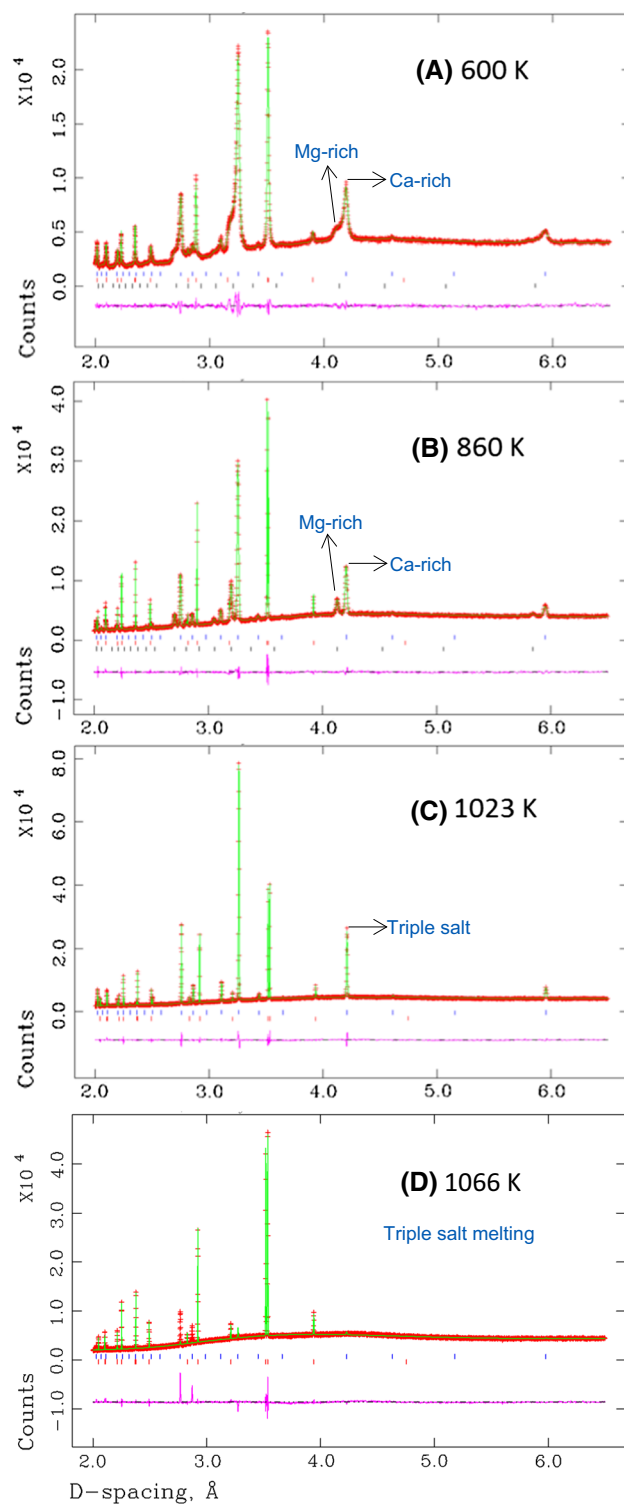


Fig. 7 Fitted synchrotron XRD patterns of langbeinite and anhydrite at **a** 600 K, **b** 860 K, **c** 1023 K and **d** 1066 K. Note the two langbeinite phases at 600 and 860 K were combined into a single-phase, triple salt, at 1023 K. At 1066 K, the triple salt started to melt, and only a limited number of grains remained, resulting in a poor fit of the langbeinite peaks. Data are shown as *plus signs*, and the *solid curve* is the best fit to the data. *Tick marks* below the pattern show the positions of allowed reflections, and the *lower curve* represents the difference between the observed and calculated profiles

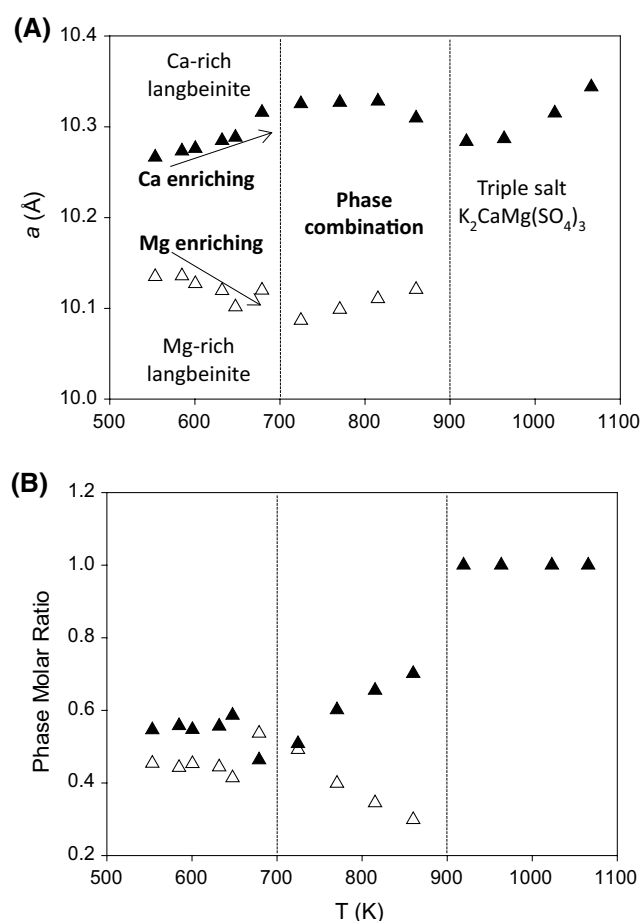


Fig. 8 Variations of **a** unit-cell parameter a and **b** molar ratio of two langbeinite solid solution phases and their combined triple salt as a function of temperature

phase indicate that it became even richer in Mg (and poorer in Ca), the effect of which overwhelmed that due to thermal expansion. Correspondingly, the Ca-rich phase became even richer in Ca (and poorer in Mg), which contributed to its increases in a (in addition to the thermal expansion effect). In other words, the differences in Ca/Mg ratio between the two phases became larger. However, on further increasing the temperature to 860 K, the a values of the Mg-rich phase increased, apparently due to lattice thermal expansion. In the meantime, the content of the Mg-rich phase decreased while that of the Ca-rich phase increased, suggesting gradual incorporation of the Mg-rich phase into the Ca-rich phase. As a result, the a values of the Ca-rich phase increased much more slowly or even decreased due to the opposite effects of thermal expansion and Mg incorporation on the dimensions of langbeinite lattice. It should be pointed out that because of the limited resolution of the XRD data, we were not able to directly determine the Ca/Mg ratio for each phase at a given temperature from Rietveld analysis. Nevertheless, the variations in lattice

parameter a with temperature reflected the changes in Ca/Mg ratio in addition to thermal expansion. When the temperature reached 919 K, the combination of the two langbeinite phases was complete, and a single-phase triple salt, $K_2CaMg(SO_4)_3$, was formed. The increases in a in the temperature range of 919–1066 K can be explained by thermal expansion of this phase.

Conclusions

The thermal behavior of polyhalite has been investigated in the temperature range of 303–1066 K using in situ high-temperature synchrotron X-ray diffraction. At about 506 K, polyhalite started to dehydrate into anhydrite and two langbeinite solid solution phases, $K_2Ca_xMg_{2-x}(SO_4)_3$, with different Ca/Mg ratios, and no polyhalite was discerned at 600 K. With further increasing the temperature to 919 K, the two langbeinite phases were combined into the single-phase triple salt, $K_2CaMg(SO_4)_3$. Rietveld analyses of the XRD data allowed determination of structural parameters of polyhalite and its decomposed anhydrite and langbeinite phases as a function of temperature. The coefficients of thermal expansion derived indicate that the thermal expansion of both polyhalite and anhydrite is highly anisotropic. Variations in unit-cell parameters of the two langbeinite phases reveal enriching in Ca of the Ca-rich phase and concomitant enriching in Mg of the Mg-rich phase, followed by the annihilation of the Mg-rich phase by the Ca-rich phase at higher temperatures. Since polyhalite is an important hydrous mineral coexisting with halite in salt formations, these results will provide valuable information for assessing the suitability of salt repositories for storage of nuclear wastes. This is especially the case for disposal of highly radioactive, high heat-generating wastes, where the heat may cause decomposition of polyhalite and release of its water to surrounding halite, potentially affecting the repository integrity and performance.

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