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Differences on the conversion of celestite in solutions bearing monovalent ions under hydrothermal conditions

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Abstract

The replacement of SO_4^{2-} ions by monovalent ions in mineral $SrSO_4$ crystals was investigated under hydrothermal conditions by using aqueous solutions bearing F^- and OH^- ions. Experiments were conducted at various temperatures (150–250 °C) for different reaction intervals (1–96 h), with M^-/SO_4^{2-} molar ratios of 1, 5 and 10, where $M^- = F^-$ or OH^-. The celestite crystals were completely converted into SrF_2 crystals, at 200 °C using a F^-/SO_4^{2-} molar ratio = 5 for 24 h. The morphology of the converted SrF_2 crystals indicated that the heteroionic conversion proceeded by a pseudomorphic replacement process, because the transformed crystals maintained their original shape and dimensions. In contrast, the $SrSO_4$ crystals were instantaneously converted into the $Sr(OH)_2$ phase by a bulk dissolution–recrystallization mechanism, resulting in the formation of large transparent acicular $Sr(OH)_2$ crystals. The differences on the conversion process are mainly associated with the chemical interaction between the mineral crystal and the hydrothermal fluid. In addition, the chemical stability of the converted phase with low solubility is also essential for the heteroionic conversion to proceed by the pseudomorphic replacement process.

Keywords: Hydrothermal treatment; Mineral celestite; Pseudomorphic replacement process; Direct conversion; Dissolution–precipitation mechanism

1. Introduction

Hitherto, one process that has been the subject of much research work in mineral celestite ($SrSO_4$), is the related with the ion exchange reaction of SO_4^{2-} ions with CO_3^{2-} ions, in order to transform $SrSO_4$ into $SrCO_3$, because the $SrCO_3$ is widely used for the preparation of strontium inorganic compounds [1–4]. The first evidences for the ion exchange process in mineral celestite, from a thermodynamic and kinetic point of view, were reported by Iwai et al. [5], who studied its leaching at low temperatures (55 °C). The exchange of SO_4^{2-} with CO_3^{2-} ions in large bulk crystal plates is achieved by two reaction mechanisms, which involve a superficial reaction and the diffusion of SO_4^{2-} ions through the dense $SrCO_3$ layer produced during early and intermediate steps of reaction [5]. Furthermore, Yoshino et al. [6] found that even under hydrothermal conditions, the conversion of $SrSO_4$ to $SrCO_3$ is achieved by a solid state ion exchange mechanism.

On the other hand, it is well known that replacement reactions take place in mineral species by dissolution–recrystallization process [7–10]. One of the replacement mechanisms that occur in mineral species is known as topotaxial ion exchange, which is achieved even in alkaline hydrothermal fluids. This particular replacement mechanism proceeds with the formation of a peculiar texture, consisting of tiny tunnels randomly distributed in the converted mineral. In terms of the crystal structure, this phenomenon normally occurs when large ions are replaced with small ones [11]. Recently, the present authors found

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that the conversion of mineral $SrSO_4$ into $SrCO_3$ crystals proceeds in the same way as that reported for apatite [11], because the crystals conserve their original morphological features after the conversion [12]. However, this conversion is not achieved by the topotaxial hydrothermal ion replacement, because the formed $SrCO_3$ crystals did not conserve the crystallographic orientation of the original $SrSO_4$ single crystals. Therefore, the conversion of mineral $SrSO_4$ into $SrCO_3$ was associated with a pseudomorphic replacement process which is achieved by a typical dissolution–precipitation mechanism.

In accordance with the former information, not many research works related with the replacement of anionic species with different electrical valence, i.e. bivalent SO_4^{2-} anions with monovalent anions (F^- or OH^-), have been conducted in mineral species such as $SrSO_4$ [13]. Hence, in the present study we have aimed to determine aspects related with the chemical stability of mineral $SrSO_4$ (celestite) in hydrothermal fluids bearing monovalent ions (F^- or OH^-), as well as to evaluate the feasibility for replacing SO_4^{2-} ions by either F^- or OH^- ions in natural $SrSO_4$ single crystals under hydrothermal conditions. Additional details regarding the reaction paths and morphological differences observed between the conversions in solutions containing monovalent (F^- and OH^-) ions are discussed on terms of the structural changes and chemical reactivity of the mineral celestite in the alkaline hydrothermal fluids.

2. Experimental procedure

Single crystals of mineral celestite were obtained from typical mineral ores in a mining area of Coahuila, Mexico. Raw mineral single crystals were cut parallel to the cleavage plane (001) direction with a diamond disk to obtain 10 mm wide and 3 mm thick square plates. These plates were washed with deionized water and cleaned using ultrasonic equipment. The selected mineral species of celestite (orthorhombic system with a *Pnma* space group) has unit cell parameters of $a = 8.3628 \pm 0.0004$ Å, $b = 5.3511 \pm 0.0004$ Å and $c = 6.8675 \pm 0.0004$ Å. Additional wet chemical analyses were conducted in order to determine the chemical composition of the celestite crystals. The major constituents in the mineral specie were 46.61 wt% Sr, 1.33 wt% Ba, and 52.05 wt% SO_4^{2-}, which correspond to 96.8 wt% $SrSO_4$ and 2.25 wt% $BaSO_4$, whilst the minor elements found in the crystals were $CaO = 0.73$ wt%, $Fe_2O_3 = 0.189$ wt%, $MnO = 0.021$ wt%, $Al_2O_3 = 0.007$ wt%. Reagent grade NaF and NaOH (Aldrich) were used as solvent for the reaction medium.

2.1. Hydrothermal treatments

A $SrSO_4$ single crystal plate was placed at the bottom of a Teflon-lined stainless-steel vessel with inner volume of 27 ml, with subsequent addition of a solvent (NaF or NaOH) solution. These solutions were prepared from appropriate amounts of NaF or NaOH to get molar A/SO_4^{2-} ratios of 1, 5 and 10, where $A = F^-$ or OH^-. A volume of 17 ml of the solvent solution was added to the vessel. This volume corresponds to a filling ratio of 70% of the autoclave. Conventional hydrothermal treatments were conducted at a predetermined temperature (150–250 °C) by heating the autoclave at a rate of 10 °C/min. The vessel was held at each temperature for several reaction intervals (1–96 h). After the hydrothermal treatments, the reaction products were separated from the remaining solution, and washed with deionized water in ultrasonic equipment.

2.2. Characterization

Powder X-ray diffraction analyses were employed to determine the crystalline phases and the lattice constants of the treated crystals by using an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized Cu$K\alpha$ radiation at 40 kV and 100 mA. Diffraction patterns were taken in the 10–80° 2θ range, at a scanning speed of 4°/min. The lattice parameters were calculated by the least-squares method from the diffraction peaks collected in the 2θ range of 35–55, at a scanning speed of 0.2°/min and a step sampling interval of 0.006°, using Si as internal standard. The morphology of the products was observed by scanning electron microscopy (Phillips XL30 ESEM). The samples were selected from partially and fully converted crystals, mounted in epoxy resin, and polished to a mirror-like surface. The microstructural observations were carried out at a polished surface which was perpendicular to the cleavage plane (001). The composition of the original celestite single crystals and that of the crystals after the hydrothermal treatments were determined by means of ICP chemical analyses (SPS 7000a Plasma Spectrometer). In addition, infrared absorption spectra were recorded with an AVATAR 320 E.S.P spectrometer, over a range from 4000 to 400 cm^{-1}, using 2 mg powder samples mixed with 200 mg of KBr. Prior to the analyses, the mixtures were dried overnight at 100 °C, and then pelletized in a 9 mm diameter die.

3. Results and discussion

3.1. Hydrothermal treatment of celestite crystals in NaF solutions

Experiments for the replacement of SO_4^{2-} ions of mineral celestite ($SrSO_4$) with monovalent ions (F^- or OH^-) under hydrothermal conditions were conducted to study the chemical stability of mineral celestite as well as the anionic replacements, for which the following factors were considered: temperature, reaction interval, and M/SO_4^{2-} molar ratio ($M = F^-$ or OH^-) of the ion exchange media. The results of the hydrothermal treatments are summarized in Table 1, together with the phases identified in the reaction products.

Table 1
Summary of the hydrothermal treatments of mineral celestite plates in monovalent solvents (F^- or OH^-)

Sample ID	Mineralizer	Molar ratio (M^-/SO_4^{2-}) $M = F^-$ or OH^-	Temperature (°C)	Duration (h)	Filling ratio (%)	Crystalline phases
SRF1	NaF	5	150	1	70	$SrSO_4 + SrF_2$
SRF6	NaF	5	150	24	70	$SrSO_4 + SrF_2$
SRF7	NaF	5	150	96	70	SrF_2
SRF8	NaF	5	200	1	70	$SrSO_4 + SrF_2$
SRF13	NaF	5	200	24	70	$SrSO_4 + SrF_2$
SRF14	NaF	5	200	48	70	SrF_2
SRF15	NaF	5	200	96	70	SrF_2
SRF16	NaF	5	250	1	70	$SrSO_4 + SrF_2$
SRF21	NaF	5	250	24	70	SrF_2
SRF22	NaF	5	250	48	70	SrF_2
SRF23	NaF	5	250	96	70	SrF_2
SRF24	NaF	1	250	96	70	$SrSO_4 + SrF_2$
SRF25	NaF	10	250	96	70	SrF_2
SRF27	NaF	5	250	96	40	$SrSO_4 + SrF_2$
SRF26	NaF	5	250	96	55	SrF_2
SROH1	NaOH	10	250	1	70	$SrSO_4 + Sr(OH)_2$
SROH2	NaOH	10	250	6	70	$SrSO_4 + Sr(OH)_2$
SROH3	NaOH	10	250	12	70	$Sr(OH)_2$
SROH4	NaOH	10	250	24	70	$Sr(OH)_2$
SROH5	NaOH	5	250	24	70	$Sr(OH)_2$

Preliminary experiments carried out by the present authors, which were conducted to determine some aspects of the chemical stability of celestite crystals in NaF solutions, and the feasibility to carry out the replacement of SO_4^{2-} ion by F^- were previously reported elsewhere [13]. The crystalline structural analyses conducted by X-ray powder diffraction, revealed that the mineral $SrSO_4$ crystals are chemically stable in NaF solutions under hydrothermal conditions below 150 °C. At this temperature the replacement of SO_4^{2-} with F^- ions did not proceed in the celestite crystals. In contrast, the formation of SrF_2 with Fluorite structure was found to occur rapidly above 200 °C. Furthermore, the direct conversion of $SrSO_4$ into SrF_2 was achieved by increasing the treatment parameters such as F^-/SO_4^{2-} molar ratio and the reaction interval.

In addition to the preliminary crystalline structural details determined previously [13], further details regarding the structural features of the reaction products obtained at early and intermediate stages of the hydrothermal treatments were revealed by FT-IR spectra analyses (Fig. 1). These results revealed that the incorporation of F^- ions into the celestite structure was noted by an abrupt increase in the F^- functional vibration band at $3742\,cm^{-1}$, as well as by a reduction of the SO_4^{2-} bending bands at 604 and $1137\,cm^{-1}$ [14], with increasing reaction time. These results are in good agreement with the structural variations determined by preliminary X-ray diffraction analyses [13]. However, a remaining peak located at $1137\,cm^{-1}$, corresponding to the SO_4^{2-} bending band, indicates the presence of a very small amount of SO_4^{2-} ions, which suggests that unconverted raw $SrSO_4$ was still present in the reaction products even after 24 h of reaction.

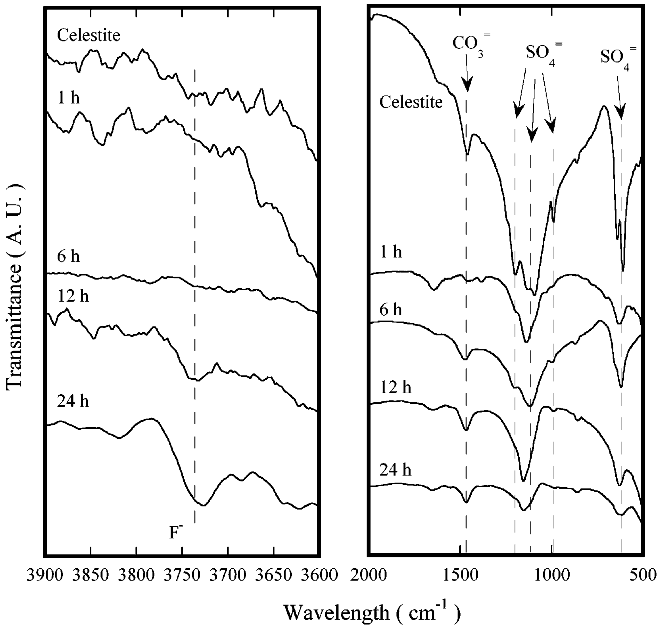

Fig. 1. Typical FT-IR spectra corresponding to partially converted SrF_2 crystals obtained by hydrothermal treatment for various reaction intervals at 250 °C in a NaF solution with a F^-/SO_4^{2-} molar ratio = 5.

On the other hand, the celestite crystals which were transformed into SrF_2 retained their original macroscopic shape and dimensions. The SEM images on Fig. 2 show typical morphologies of fully converted SrF_2 crystals for 24 and 96 h at 250 °C in a NaF solution with a molar F^-/SO_4^{2} ratio of 5. Although the macroscopic aspect of the crystals remained unchanged after the reaction, the microstructure

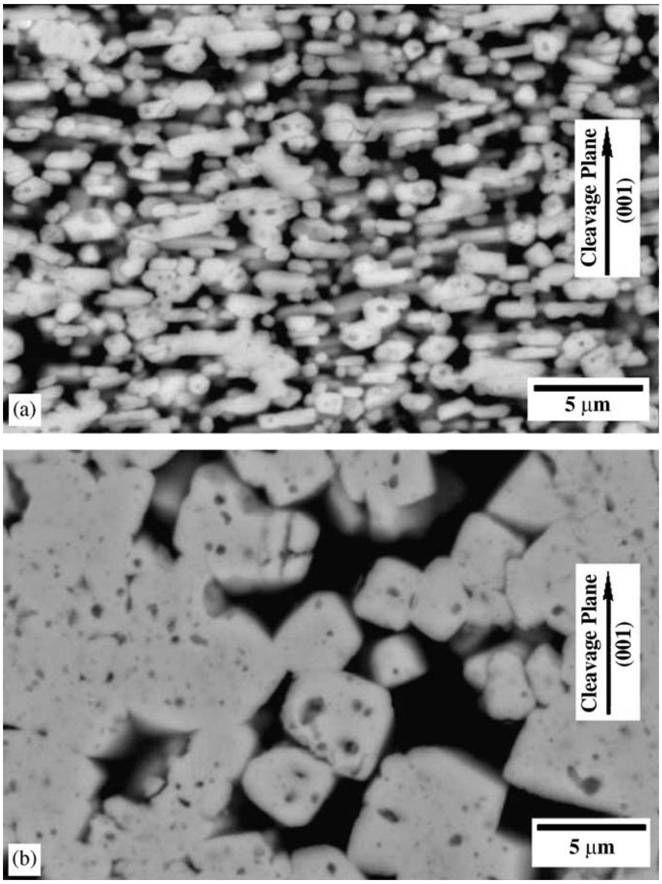

Fig. 2. SEM images of a cross section perpendicular to the cleavage plane (001) of SrF_2 crystals converted at 250 °C in a NaF solution with a F^-/SO_4^{2-} molar ratio = 5, for reaction intervals of: (a) 24 h and (b) 96 h.

of the SrF_2 crystal converted at an intermediate stage of reaction (24 h, Fig. 2a) consisted of very tiny elongated particles (up to 3 μm long) and a significant amount of interconnected large pores. When the crystals were treated for a longer reaction interval (96 h), the microstructure of the reaction product had marked differences in shape and size with respect to the SrF_2 phase obtained after 24 h of treatment. The small SrF_2 elongated particles were morphologically transformed into well-defined pseudo-cubic grains grown to a size of approximately 10 μm. Simultaneously, a rearrangement of the porosity also occurred (Fig. 2b). These results suggest that even the new SrF_2 phase is not chemically stable in NaF solutions, and it was dissolved and recrystallized during the hydrothermal treatments conducted for a long time over 96 h. The bulk morphology of fully converted crystals obtained for the longest reaction interval (96 h) did not change in comparison with those corresponding to the original celestite crystals.

In an ordinary hydrothermal treatment, especially when it is conducted with a temperature gradient, mass transport is achieved by convection of the hydrothermal fluid. Under these conditions, new crystals are produced in a different place of the reaction vessel by a dissolution and precipitation mechanism [11,15]. In our study, the complete dissolution of original $SrSO_4$ and converted SrF_2 crystals did not occur even during long-term reaction experiments. The fact that the converted SrF_2 crystals maintained their original shape and dimensions after the hydrothermal treatment might be explained by the low solubility of SrF_2 in the hydrothermal fluid (NaF). Thus, the SrF_2 crystals with low solubility were crystallized just at the reaction front maintaining the original shape of the raw crystal [7,16].

Details regarding the kinetic aspects of the conversion of $SrSO_4$ into SrF_2 are given in Fig. 3. The curves plotted were determined by systematic measurements (30 times) of the reacted layer thickness, on crystals treated in NaF solutions with a F^-/SO_4^{2-} molar ratio of 10, at several reaction temperatures. In general, the conversion reaction proceeded rapidly only in those crystals treated above 200 °C for reaction intervals up to 12 h; then, the rate of conversion was slightly slowed down by increasing the reaction interval above 24 h. The present results indicate that under these conditions a large-scale conversion of celestite into SrF_2 crystals proceeds rapidly at a relatively low temperature (200 °C). However, the replacement of SO_4^{-2} by F^- ions was also completed for the longest reaction interval (96 h) at a temperature of 150 °C. These results may be associated with a variation on the reactivity of $SrSO_4$ in the NaF solution under hydrothermal conditions, because this factor affects the solid dissolution rate as well as the saturation rate of the solvent. This factor could account for the difference on the replacement reaction kinetics observed between the crystals treated at

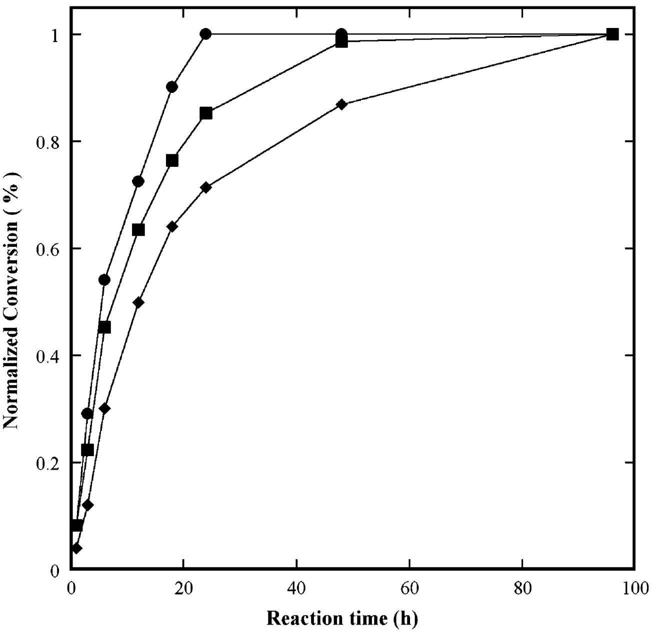

Fig. 3. Conversion rate curves determined for partially and fully converted $SrSO_4$ crystals treated in a NaF solution with a F^-/SO_4^{2-} molar ratio = 10, at a temperature of: (◆) 150 °C, (■) 200 °C, and (●) 250 °C.

Table 2
Summary of the lattice parameters determined on fully converted SrF_2 crystals and $Sr(OH)_2$ small crystals, which were obtained under hydrothermal treatments in NaF and NaOH solutions, respectively

Sample ID	Mineralizer	Molar ratio (M^-/SO_4^{2-}) $M = F^-$ or OH^-	Temperature (°C)	Duration (h)	Filling ratio (%)	Lattice parameters			Cell volume (Å^3)
						a (Å)	*b* (Å)	*c* (Å)	
SRF7	NaF	5	150	96	70	5.8027			195.38
SRF14	NaF	5	200	48	70	5.8013			195.24
SRF15	NaF	5	200	96	70	5.8012			195.23
SRF21	NaF	5	250	24	70	5.8019			195.30
SRF22	NaF	5	250	48	70	5.8015			195.26
SRF23	NaF	5	250	96	70	5.8009			195.21
SRF25	NaF	10	250	96	70	5.8009			195.22
SRF26	NaF	5	250	96	55	5.803			195.45
SROH3	NaOH	10	250	12	70	6.2013	9.9515	3.943	243.33
SROH4	NaOH	10	250	24	70	6.1503	9.8901	3.915	240.47
SROH5	NaOH	5	250	24	70	6.1612	9.9212	3.934	238.14
		Celestite (JCPDS card 05-0593)				8.4328	5.3940	6.8675	312.38
		Strontium Fluoride (JCPDS card 06-0262)				5.800			195.11
		Barium Fluoride (JCPDS card 04-0452)				6.2002			238.35
		Strontium Hydroxide (JCPDS card 05-0418)				6.1201	9.892	3.9193	237.27

low (150 °C) and high (>200 °C) temperatures, i.e., this could be explained by the fact that the dissolution is limited by a low chemical reactivity of the $SrSO_4$ crystals in contact with a saturated NaF solution ($F^-/SO_4^{2-} = 10$). This particular condition must occur on the experiments conducted at low temperatures (150 °C). In addition, morphological details regarding the reaction pattern revealed that in our case the conversion is similar to that established for a pseudomorphical replacement process, which involves a moving reaction front with a simultaneous formation of an inner residual porosity [17].

3.2. *Lattice parameters of the hydrothermally converted strontium fluoride crystals*

The variation of the lattice parameters, determined based on the cubic cell symmetry, was calculated for the SrF_2 crystals obtained at various reaction intervals and different treatment temperatures, these results are summarized in Table 2. The measurements conducted on SrF_2 specimens converted at 250 °C for various reaction intervals with a F^-/SO_4^{2-} molar ratio of 5, revealed that the "*a*" lattice parameter decreased from 5.8019 ± 0.0009 to 5.8009 ± 0.0009 Å by increasing the reaction interval from 24 to 96 h. However, only a slight reduction on the "*a*" value of the SrF_2 phase was determined for crystals treated at reaction intervals longer than 48 h. Above 48 h, no significant variations on the "*a*" lattice parameter of the converted SrF_2 crystalline phase were determined. The SrF_2 phase obtained by treatments longer than 48 h had an average "*a*" lattice parameter value of 5.8009 ± 0.0009 Å which is similar to that of the SrF_2 compound (5.80 Å, Table 2). In addition, no significant variations on the "*a*" lattice parameter were observed on the SrF_2 crystals converted at low temperature (200 °C, sample ID *SRF15*) for 96 h, when compared with the values obtained for the specimens prepared at 250 °C, sample ID *SRF23*. The "*a*" value of 5.8012 ± 0.0009 Å determined for the SrF_2 phase obtained at 200 °C, is similar to that determined for the SrF_2 crystals converted at 250 °C.

In general, the values of the lattice parameter determined for the reaction products obtained in treatments conducted for long reaction intervals (>24 h) in NaF solutions, are similar to that corresponding to pure SrF_2, even though the raw celestite crystals contained a small amount of barium (1.33 wt%). The variation of lattice parameter (Table 2) bears a clear evidence indicating that a purification process proceeds simultaneously to the conversion of $SrSO_4$ by SrF_2. Additionally, chemical compositional analyses conducted by ICP on raw celestite crystals, as well as on the converted SrF_2 crystals were carried out in order to provide more details on the purification process. The results given in Table 3 clearly show that the content of Ba in the converted SrF_2 crystals was gradually decreased by increasing both reaction time and temperature. Therefore, these results suggest that the removal of Ba proceeded simultaneously to the pseudomorphic hydrothermal conversion process. In fact, the purification of mineral species is a common process that occurs under hydrothermal conditions, when the mineral is simultaneously dissolved and recrystallized [12].

3.3. *Hydrothermal treatment of celestite crystals in NaOH solutions*

A preliminary treatment conducted to evaluate the chemical stability of $SrSO_4$ crystals in OH^- bearing media, was carried out using pure water at 250 °C for 24 h. After the treatment, the crystals retained the original orthorhombic structure of $SrSO_4$, and no changes on morphology

Table 3
Strontium and barium content of celestite single crystal samples hydrothermally treated with NaF solutions

Sample ID	Temperature (°C)	Time (h)	Filling ratio (%)	Molar ratio (F^-/SO_4^{2-})	Chemical composition (wt%)				Chemical formula
					Sr	Ba	SO_4^{2-}	F^{-a}	
Celestite					46.6(5)	1.3(5)	52.0(5)		$Sr_{0.98}Ba_{0.02}SO_4$
SRF14	200	48	70	5	46.7(7)	1.0(7)		52.1(7)	$Sr_{0.98}Ba_{0.02}F_2$
SRF22	250	48	70	5	46.8(5)	0.9(5)		52.1(5)	$Sr_{0.98}Ba_{0.02}F_2$
SRF30	250	72	70	5	47.1(3)	0.5(3)		52.3(3)	$Sr_{0.99}Ba_{0.01}F_2$
SRF23	250	96	70	5	47.3(3)	0.2(3)		52.4(4)	$Sr_{0.99}Ba_{0.01}F_2$

[a] Fluorine contents were determined from the dissolved crystals by wet chemistry using an ion chromatograph apparatus with a F^- standard solution.

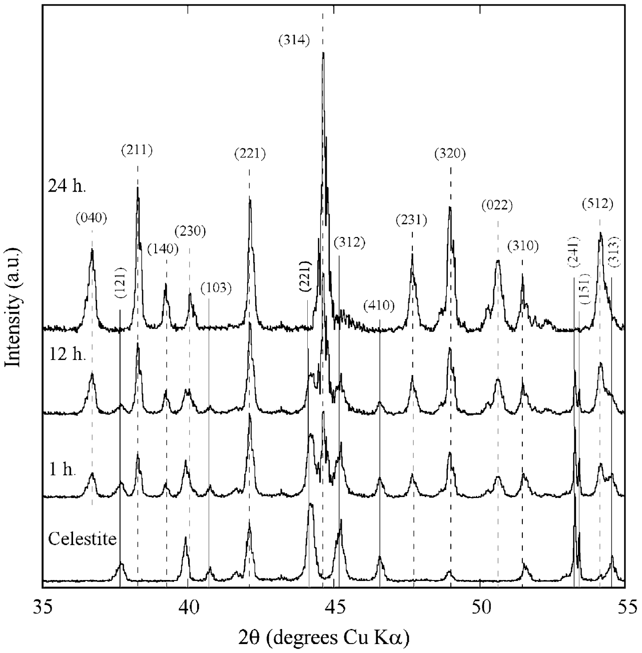

Fig. 4. (a) X-ray diffraction pattern of the reaction products obtained by hydrothermal treatments conducted in a NaOH solution with a OH^-/SO_4^{2-} molar ratio = 10, after several reaction intervals at 250 °C.

or size of the original crystals were determined by naked eye observations. Similar results were obtained for hydrothermal treatments conducted using an alkaline NaOH solution with a OH^-/SO_4^{2-} molar ratio of 1. In contrast, when the celestite crystals were treated in concentrated alkaline NaOH solutions (with OH^-/SO_4^{2-} molar ratios of either 5 or 10), it was found that the celestite crystal was dissolved in the hydrothermal fluid, resulting in the formation of a small amount of regular-shaped small crystals as well as in a fine powder found at the vessel bottom. Typical X-ray diffraction patterns of the reaction products (acicular crystals and fine powder) obtained at 250 °C in a NaOH solution with a OH^-/SO_4^{2-} molar ratio = 10, for various reaction intervals, are shown in Fig. 4. The diffraction patterns of the reaction products were indexed with that corresponding to monoclinic strontium hydroxide ($Sr(OH)_2$, JCPDS card 27-1438).

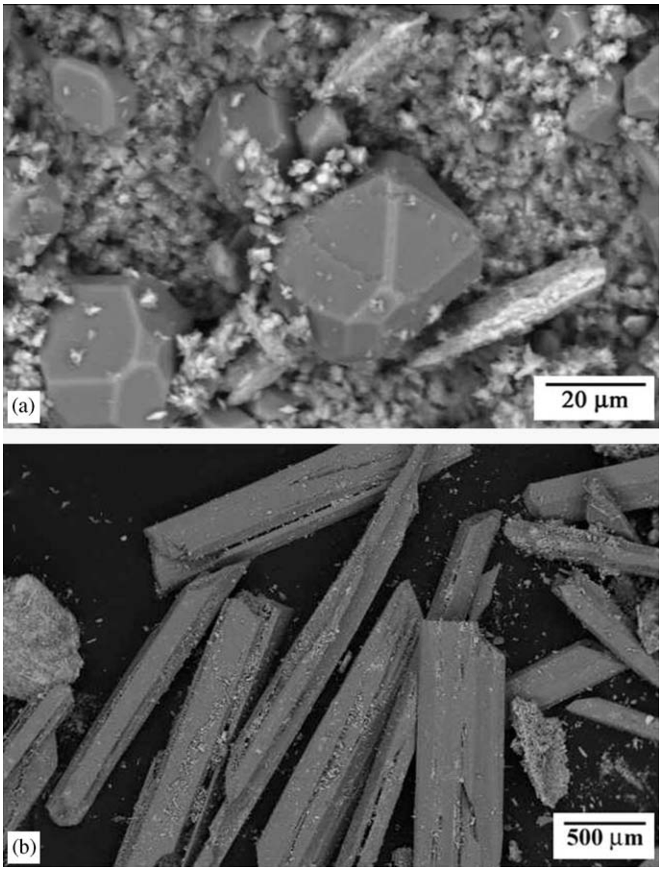

Fig. 5. Typical SEM micrographs of the small $Sr(OH)_2$ crystals obtained after hydrothermal treatments in a NaOH solution (OH^-/SO_4^{2-} molar ratio = 10) at 250 °C, for (a) 6 h and (b) 24 h, respectively.

The facts mentioned above were elucidated by SEM observations conducted on the reaction products obtained under hydrothermal conditions at 250 °C in a highly concentrated NaOH solution (OH^-/SO_4^{2-} molar ratio = 10), for several reaction intervals. Fig. 5a shows that a small number of particles with a regular (polyhedral) morphology and some markedly agglomerated fine particles were obtained after 6 h of reaction. Both reaction products were found to correspond to $Sr(OH)_2$. A small portion of the original $SrSO_4$ crystals was also found mixed with the $Sr(OH)_2$ particles. In contrast, a large number of long prismatic $Sr(OH)_2$ crystals were produced during the treatments carried out at the longest reaction interval considered (96 h), these crystals were formed in the whole inner vessel volume. We suggest that the long $Sr(OH)_2$ crystals may be formed due to a severe bulk dissolution of the remaining original $SrSO_4$ crystal, as well as by dissolution of the small $Sr(OH)_2$ crystals obtained at the early stages of reaction. This process might occur due to the high concentration of the alkali hydrothermal media employed [15]. Furthermore, the growth of bulky crystals proceeded very slowly because of the slow conversion rate of $SrSO_4$ into $Sr(OH)_2$. In consequence, different growth conditions might be produced during the hydrothermal treatment inside the vessel, which led to the morphological change of the $Sr(OH)_2$ crystals obtained for intermediate reaction intervals (24 h).

3.4. Differences on the conversion process of mineral celestite in hydrothermal fluids bearing monovalent ions

Some details of the course for the conversion of $SrSO_4$ into SrF_2 were investigated on the cross section of partially converted crystals at 250 °C for 6 h, employing a F^-/SO_4^{2-} molar ratio = 10. Fig. 6 shows a typical SEM image taken on a direction normal to the cleavage plane (001) of the celestite crystal. In this image, four different areas are visible on the microstructure of the partially reacted $SrSO_4$ crystal. A continuous phase with a smooth surface remained inside the crystal (left-hand side part of Fig. 6); which corresponds to the original celestite crystal as was reveled by punctual X-ray energy dispersive analyses. Furthermore, the formation of a crevasse that separates the unreacted and reacted zones was a peculiar feature of the conversion (Fig. 6). The reacted zone is formed by a thin layer of relatively dense aggregated crystals, as well as by an outer thick layer consisting of small elongated crystals with some randomly distributed pores, these crystals corresponded to the fully converted SrF_2 crystalline phase. From these results, we suggest that the sharp crevasse formed at the reaction front resulted from a marked volumetric contraction [13]. Furthermore, the peculiar reaction pattern revealed at the reaction front is very similar to that determined for a mineral pseudomorphic replacement process. This particular replacement process involves a moving reaction front, which can be either a thin crevasse where a fluid film can penetrate or interconnected porosity [16,17]. In addition, preliminary sulfur compositional evaluations conducted across the reaction interface showed that the conversion of $SrSO_4$ into SrF_2 proceeded very fast without bearing evidences of a sulfur concentration gradient, even at low temperatures (150 °C) [13]. Hence, this typical heteroionic conversion of $SrSO_4$ into SrF_2 is mainly achieved by a coupled bulk dissolution–precipitation mechanism of ionic species [7–10] rather than by a topotaxial hydrothermal ion exchange mechanism [11], because the converted products were not single crystals and the formation of a solid solution phase at intermediate stages of conversion was not observed.

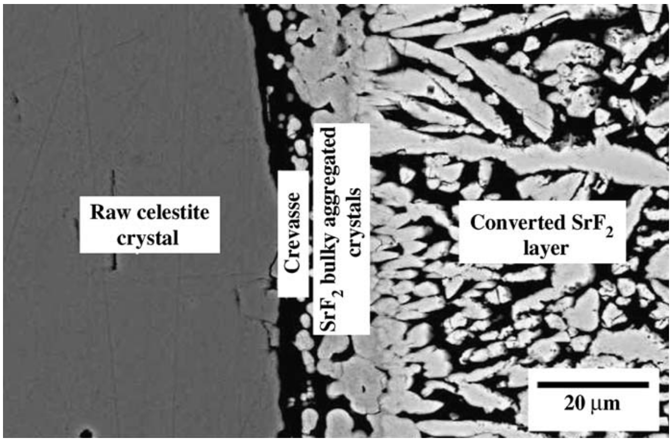

Fig. 6. Typical SEM image of the reaction interface determined on partially converted $SrSO_4$ crystals obtained at 250 °C after 6 h in a NaF solution with a F^-/SO_4^{2-} molar ratio = 10.

In contrast with the above described conversion process, the celestite crystals treated under alkaline hydrothermal conditions were completely damaged when high concentrated NaOH solvents were used (with OH^-/SO_4^{2-} molar ratios of 5 or 10) for very short reaction intervals (1 h). As a result, small transparent crystals were obtained inside the whole vessel volume (Fig. 5). However, the present experimental results showed that the pseudomorphic conversion of $SrSO_4$ into $Sr(OH)_2$ is not able to proceed by a replacement process similar to those occurring in a broad number of mineral species, namely topotaxial ion-exchange [11] or pseudomorphic dissolution–precipitation [7].

In this particular case, the pseudomorphic replacement process may be further limited by two factors: (a) the high chemical stability of the mineral $SrSO_4$ in dilute NaOH solutions and (b) a very high solubility of the $Sr(OH)_2$ phase in concentrated NaOH solutions under hydrothermal conditions. These two factors seem to affect the equilibrium condition for the dissolution and precipitation rates required for a pseudomorphic replacement mechanism in mineral species. The mineral celestite underwent a sever dissolution process in concentrated NaOH solutions followed by the nucleation and growth of $Sr(OH)_2$ crystals in the solution. Indeed, mineral species undergo bulk dissolution when they exhibit a low chemical stability in hydrothermal fluids. In some species the dissolution proceeds anisotropically, resulting in the complete dissolution of the mineral species [10], as for the case of the conversion process of $SrSO_4$ into $Sr(OH)_2$.

In general, the pseudomorphic replacement has been determined to proceed in some mineral-aqueous solution systems without disruption of bulk morphology or major crystalline structural changes in the mineral [7,16]. These particular features of the pseudomorphic conversion process are commonly affected by the type of ions that are involved on the replacement process, thus, the mineral conversion is mainly promoted by the exchange of elements with similar chemical properties, namely electric valence [7]. However, the present results demonstrate that a heteroionic conversion is also able to occur in mineral species under hydrothermal conditions by a pseudomorphic replacement process. Additionally, the typical texture consisting of small crystals with pores, developed during the heteroionic conversion of mineral $SrSO_4$ into SrF_2, is similar to that obtained for mineral species in which the exchanged ions had no difference in their electrical valance [16]. Finally, in accordance with our results for the conversions studied, $SrSO_4$ into SrF_2 or $SrSO_4$ into $Sr(OH)_2$, we surmise that for a conversion process to occur in mineral species, some factors are required in order to achieve the pseudomorphic replacement process under hydrothermal conditions. The original mineral specie (crystal) should have a moderate chemical reactivity with the reaction medium, while a molar volume reduction in the converted crystal structure is necessary to produce reaction flow paths in order to promote fluid media exchange inside and outside the crystal. In addition, the stability (low solubility) of the products is also required in order to maintain the bulk shape and dimensions of the original crystals. The present experimental results demonstrate that only the conversion of $SrSO_4$ to SrF_2 satisfies these factors. In contrast with that of $SrSO_4$ to $Sr(OH)_2$, in which the second factor was not met because the solubility of the $Sr(OH)_2$ product is too high. This phenomenon impeded the formation of $Sr(OH)_2$ at the reaction front due to the complete dissolution of the Sr species at that place.

4. Conclusions

The present experimental results demonstrate that the heteroionic conversion of mineral $SrSO_4$ (celestite) crystals (10 mm wide and 3 mm thick square plates) is able to proceed under hydrothermal conditions, at a temperature range over 150–250 °C. The $SrSO_4$ crystals were pseudomorphically converted into SrF_2 crystals in NaF solutions by means of a dissolution–crystallization mechanism. Furthermore, the pseudomorphic replacement of SO_4^{2-} ions by F^- ions was accelerated by increasing the reaction temperature and F^-/SO_4^2 molar ratio. In contrast, the heteroinic conversion of $SrSO_4$ crystals into $Sr(OH)_2$, was further limited even in highly concentrated alkaline media (NaOH solutions, OH^-/SO_4^{2-} molar ratio $= 10$) under hydrothermal conditions. The $SrSO_4$ crystals were markedly dissolved into the alkaline solvent, resulting in the subsequent crystallization of long acicular crystals of $Sr(OH)_2$. In general, in order to achieve the heteroionic pseudomorphic conversion of a mineral specie, this should have a moderate chemical reactivity with the hydrothermal fluid medium, and a molar volume reduction must also proceed in the solid to produce reaction flow paths during early and intermediate stages of reaction. In addition, the reaction products must be chemically stable (low solubility) in the hydrothermal media in order to maintain the bulk shape and dimensions of the original mineral specie.

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