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The conversion of mineral celestite to strontianite under alkaline hydrothermal conditions

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Abstract

The exchange of SO_4^{2-} ions with CO_3^{2-} ions in natural strontium sulfate (celestite) single crystals was investigated under alkaline hydrothermal conditions. The hydrothermal treatments were conducted using a stainless steel Teflon-lined vessel. Experiments were performed at different temperatures from 150 to 250 °C for various reaction times between 1 and 96 h with a molar ratio of $CO_3^{2-}/SO_4^{2-} = 1, 5$ and 10. Structural characterization of partially and completely converted strontianite ($SrCO_3$) crystals was conducted by XRD, FTIR and SEM. X-ray diffraction results showed that under hydrothermal conditions the exchange of CO_3^{2-} ions in celestite was completed at 250 °C in a Na_2CO_3 solution with a molar ratio $CO_3^{2-}/SO_4^{2-} = 10$ for 96 h, and celestite changed to strontianite. The morphology of the converted strontianite crystals depicted that the conversion proceeds without severe changes of the original shape and dimension of the crystals. A peculiar texture, however, consisting of elongated channels and tiny holes distributed randomly normal to the (001) cleavage plane, was formed in order to compensate the dimensional change of the lattice parameters associated with the conversion of celestite to strontianite. Details regarding the conversion mechanism are discussed in the present work.

1. Introduction

The exchange reaction of SO_4^{2-} ions of celestite with CO_3^{2-} has been the subject of many research works over the last century, because celestite is the important mineral species of strontium, which is the raw material to prepare strontium inorganic compounds [1–3]. Recently, the leaching of celestite particles and crystal plates ($10 \times 10 \times 10$ mm^3) was found to proceed in sodium carbonate solutions at very low temperatures under atmospheric pressure [4].

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Iwai *et al* [4] studied the leaching from a thermodynamic and kinetic point of view, and reported that the exchange of SO_4^{2-} ions with CO_3^{2-} in large bulk crystal plates is achieved by two mechanisms. An initial reaction involves a surface reaction. The second mechanism proposed is related to the diffusion of SO_4^{2-} ions through a dense strontium carbonate layer produced at the earlier stage of the conversion process [4]. In addition, other investigations reported that the leaching reaction in celestite particles which leads to the conversion to strontianite is achieved by a topo-chemical ion-exchange mechanism [5, 6]. However, the above-cited references did not report the details on the effect of the crystallographic structural changes associated with the conversion of celestite to strontianite. In contrast, Yoshino *et al* [7] found the first evidence that, even under hydrothermal conditions, the conversion of celestite to strontianite is achieved by a solid state ion-exchange mechanism. The ion exchange in the solid state is faster under hydrothermal conditions at pressures between 1 and 100 MPa, and the interface of the reaction in the celestite crystal remains smooth, bearing a SO_4^{2-} concentration gradient. This fact was also confirmed by Brenan [8], who determined the influence of pressure on the diffusion coefficients of anions in mineral apatite during hydrothermal treatments.

On the other hand, it is well known that replacement reactions in mineral species take place by dissolution–recrystallization processes [9, 10]. Recently, it has been found that in alkaline hydrothermal fluids, the topotaxial replacement of ions in mineral species is enhanced by the formation of a peculiar texture, consisting of tiny tunnels randomly distributed in the converted mineral. Yanagisawa *et al* [11] proposed that the texture was formed at the conversion of chlorapatite to hydroxyapatite in order to compensate the dimensional change that resulted from the structural conversion, mainly when large ions are exchanged with small ones. However, an anisotropic dissolution process which depends on the reactivity of the mineral species with the hydrothermal fluid produced very large holes in the converted mineral species when chlorapatite was converted to fluorapatite [12]. In addition, an important observation made on the ion exchange of Cl^- ions with OH^- ions, was that a chlorapatite single crystal was converted to a hydroxyapatite single crystal. Under alkaline hydrothermal conditions, the topotaxial ion-exchange process is achieved by a mechanism of dissolution and precipitation of clusters, species much larger than ionic species. The uptake of OH^- ions and the release of Cl^- take place at the surface of the clusters, which are then reassembled to form the new single crystal [11]. According to the former information, we expect that the ion exchange of SO_4^{2-} ions with CO_3^{2-} ions is likely to occur in mineral celestite single crystals under alkaline hydrothermal conditions bearing a highly concentrated carbonate ion-exchange medium. Initial attempts were made to determine the differences on the conversion of celestite to strontianite by using two anion-exchange media, Na_2CO_3 and K_2CO_3.

2. Experimental procedure

2.1. Materials

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 disc, in order to obtain square plates with the dimensions of 10 mm width and 3 mm thickness. These plates were washed with deionized water and cleaned using an ultrasonic equipment. X-ray analyses (figure 1(a)) revealed that the celestite single crystals belong to the orthorhombic system with the space group *Pnma* with unit cell parameters $a = 8.3628 \pm 0.0004$ Å, $b = 5.3511 \pm 0.0004$ Å and $c = 6.8675 \pm 0.0004$ Å. The chemical composition of the celestite crystals was determined by wet chemistry analyses, which show that the major constituents are: Sr = 44.93 wt%, Ba = 3.83 wt% CO_3 = 1.22 wt% and

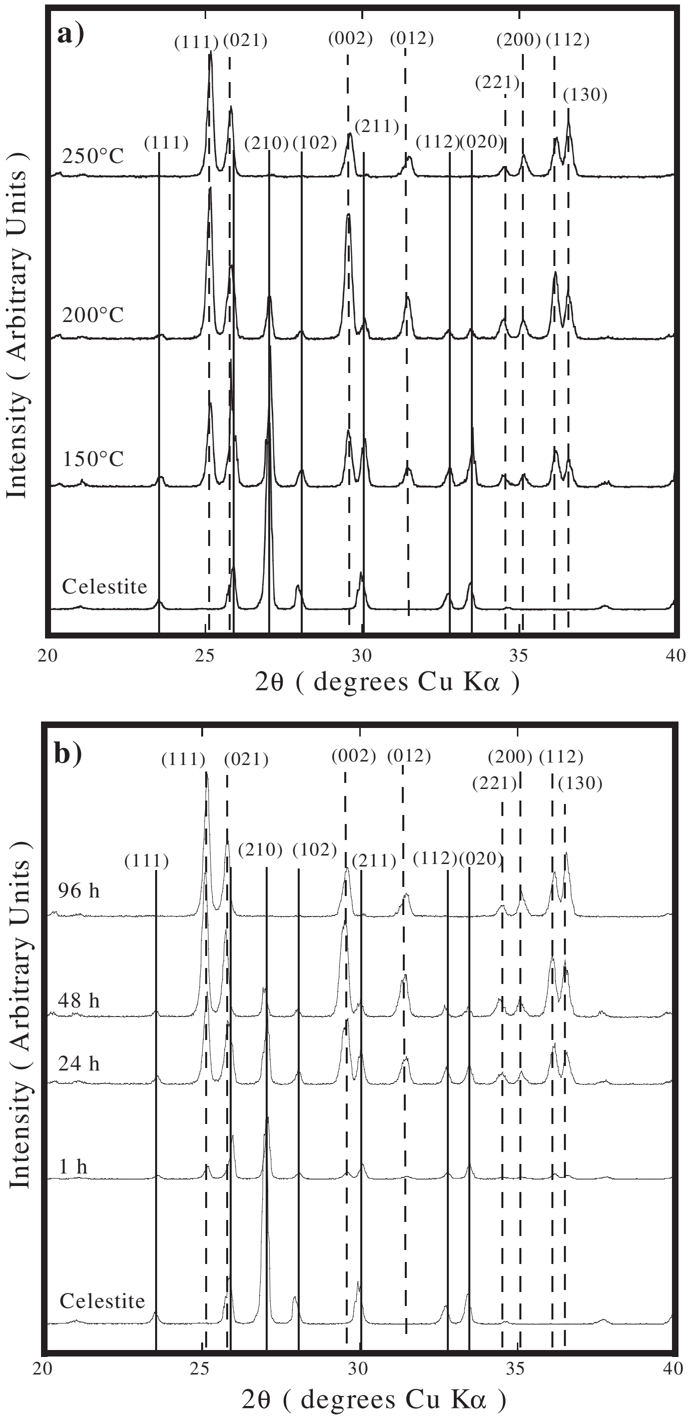

Figure 1. XRD patterns of the specimens obtained from the celestite crystals after hydrothermal treatments in an Na_2CO_3 solution (a) with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 for 96 h at various temperatures; (b) with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 at 250 °C for various times, and (c) at 250 °C for 96 h with different CO_3^{2-}/SO_4^{2-} molar ratios. Dotted lines = strontianite; solid lines = celestite.

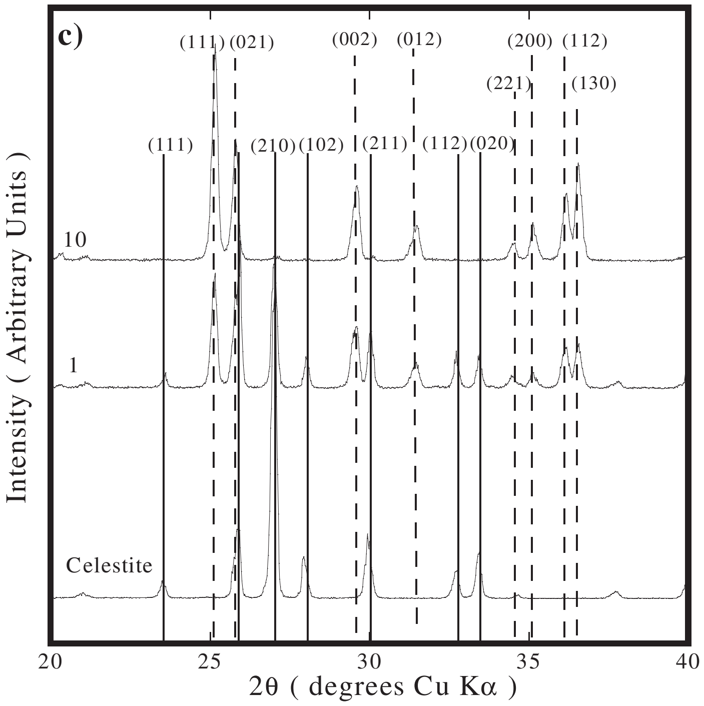

Figure 1. (Continued.)

$SO_4 = 49.98$ wt%; this corresponds to $SrSO_4$ 90.0 wt%, $SrCO_3$ 3 wt% and $BaSO_4$ 6.5 wt%. Fluid mineralizers prepared from reagent grade Na_2CO_3 and K_2CO_3 (Aldrich) were used as ion-exchange media.

2.2. *Hydrothermal treatments*

A celestite ($SrSO_4$) crystal plate (approximately 0.5 g) was placed at the bottom of a Teflon-lined stainless steel vessel with inner volume of 27 ml, and then the mineralizer, Na_2CO_3 or K_2CO_3, was added to get three different CO_3^{2-}/SO_4^{2-} ratios (1, 5 and 10) with 17 ml of deionized water for a 70% fill ratio. The conventional hydrothermal treatments were conducted at a predetermined temperature (150–250 °C) by heating the vessel at a rate of 10 °C min^{-1}. The vessel was held at each temperature for several reaction times (1–96 h). The cooling stage was conducted by using an electric fan. After the hydrothermal treatments, the reaction products were washed with deionized water in an ultrasonic equipment.

2.3. *Characterization*

Powder x-ray diffraction analyses were employed to determine the crystalline phases and the lattice constants of the treated crystals using an x-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized Cu Kα radiation at 40 kV and 100 mA. Diffraction patterns were taken in the 2θ range from 10° to 80° at a scanning speed of 4° min^{-1}. The lattice parameters were calculated by the least-squares method from the diffraction peaks collected in the 2θ range from 35° to 55° at a scanning speed of 0.2° min^{-1} and step sampling interval of 0.006°, using Si as an internal standard. The morphology of the products was observed by scanning electron microscopy (Philips XL30 ESEM). To determine the reaction process, compositional analyses of sulfur were conducted, using an energy dispersive x-ray device. The samples were selected from partially and completely converted crystals, after the crystals were mounted in epoxy resin and polished to a mirror-like surface. The surfaces observed were perpendicular to the cleavage plane (001). In addition, infrared absorption spectra were recorded with an AVATAR 320 E.S.P spectrometer, over the range from 4000 to 400 cm^{-1} using 2 mg of a powder sample mixed with 200 mg of KBr. Prior to the analyses the mixture was dried at 100 °C, and then pelletized in a 9 mm diameter die.

3. Results and discussion

3.1. Hydrothermal treatments in Na_2CO_3 solutions

Experiments for the conversion of celestite ($SrSO_4$) to strontianite ($SrCO_3$) under hydrothermal conditions were conducted by considering the effect on the exchange of SO_4^{2-} ions with CO_3^{2-} ions by the following factors: temperature, reaction time, and the molar ratio CO_3^{2-}/SO_4^{2-} 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.

Figure 1(a) shows x-ray diffraction patterns of the raw celestite crystals, together with those of the crystals that remained after the hydrothermal treatments at different temperatures for 96 h in an Na_2CO_3 solution with a molar ratio of $CO_3^{2-}/SO_4^{2-} = 10$. These results revealed that the exchange of SO_4^{2-} ions with CO_3^{2-} ions in celestite crystals proceeds at temperatures as low as 150 °C. After the treatments at low temperatures below 200 °C, two phases were observed in the reaction products. One of these phases was the original celestite, and the new phase corresponded to strontianite (orthorhombic system, space group *Pmcn*, JCPDS card 05-0418). In contrast, when the celestite crystal plate was treated at 250 °C, celestite was completely converted to strontianite.

Figure 1(b) shows XRD patterns of crystals treated at 250 °C for several reaction times, with a molar ratio CO_3^{2-}/SO_4^{2-} of 10. From these results, one can clearly observe a trend with increasing reaction time, which is similar to that observed for increasing temperature. The formation of strontianite from celestite crystals was observed after treatment for an interval as short as 1 h. The increase in the reaction time to 96 h resulted in the complete transformation of the celestite to strontianite structure. The x-ray diffraction patterns of the products with the strontianite structure formed by a short reaction time showed a slight shifting to a higher angle, compared with those formed by a long reaction time (96 h). This displacement might be attributed to the presence of a small amount of SO_4^{2-} ions in the lattice positions of the CO_3^{2-}.

The effect of the molar ratio (CO_3^{2-}/SO_4^{2-}) value of the ion-exchange media on the XRD patterns of hydrothermally treated crystals is shown in figure 1(c). A partial conversion of the celestite occurred when the crystal was treated in an Na_2CO_3 solution at a low value of the molar ratio, $CO_3^{2-}/SO_4^{2-} = 1$. The increase of the molar ratio value to 10 resulted in the complete transformation of celestite to strontianite.

The structural changes observed in the celestite crystals treated at early and intermediate stages of the reactions by the XRD patterns are attributed to compositional variations, which can be observed by the IR spectra (figure 2). The incorporation of the CO_3^{2-} ions in the celestite structure was noted by the abrupt increase of the CO_3^{2-} functional vibration bands (at 696, 855, 1461 and 1780 cm^{-1}) and further reduction of the SO_4^{2-} bending bands at 604 and 1137 cm^{-1} [13], with increasing the reaction time (figure 2(a)) and temperature (figure 2(b)). These results are in a good agreement with the structural variations determined by x-ray analyses.

Table 1. Summary of hydrothermal treatments of celestite single crystals.

Sample ID	Mineralizer	Molar ratio CO_3^{2-}/SO_4^{2-}	Temperature (°C)	Duration (h)	Fill ratio (%)	Crystalline phases	Lattice parameters			Cell volume (Å^3)
							a (Å)	*b* (Å)	*c* (Å)	
A	Celestite (raw material)						8.4328	5.3940	6.8675	312.37
B	Na_2CO_3	10	250	1	70	$SrSO_4$ + $SSSrCO_3$[a]	5.1038	8.4405	6.0248	259.54
C	Na_2CO_3	10	250	24	70	$SSSrCO_3$[a]	5.1059	8.4091	6.0266	258.89
D	Na_2CO_3	10	250	48	70	$SSSrCO_3$[a]	5.1071	8.4091	6.0274	258.85
E	Na_2CO_3	10	250	96	70	$SrCO_3$	5.1071	8.4090	6.0275	258.85
G	Na_2CO_3	1	250	96	70	$SrCO_3$	5.1044	8.4113	6.0309	258.93
H	Na_2CO_3	10	200	96	70	$SrCO_3$	5.1104	8.4102	6.0280	259.08
H2	Na_2CO_3	10	150	96	70	$SrSO_4$ + $SSSrCO_3$[a]	—	—	—	—
I	K_2CO_3	10	250	96	70	$SrCO_3$	5.1091	8.4136	6.0283	259.13
J	K_2CO_3	10	250	24	70	$SSSrCO_3$[a]	5.1787	8.4102	6.0272	262.51
Mineral strontianite[b]							5.1070	8.4140	6.0290	259.06
Mineral celestite[b]							8.3590	5.3520	6.8660	307.16

[a] $SSSrCO_3 = CO_3^{2-}$-rich solid solution in the system $SrCO_3$–$SrSO_4$.

[b] Mineral strontianite from JCPDS card no 05-0418 (major impurities: <0.1% Ba; 0.01% Ca,); and celestite from JCPDS card no 05-0593 (major impurities: <0.1% Ba, <0.01% Na; 0.001% Al).

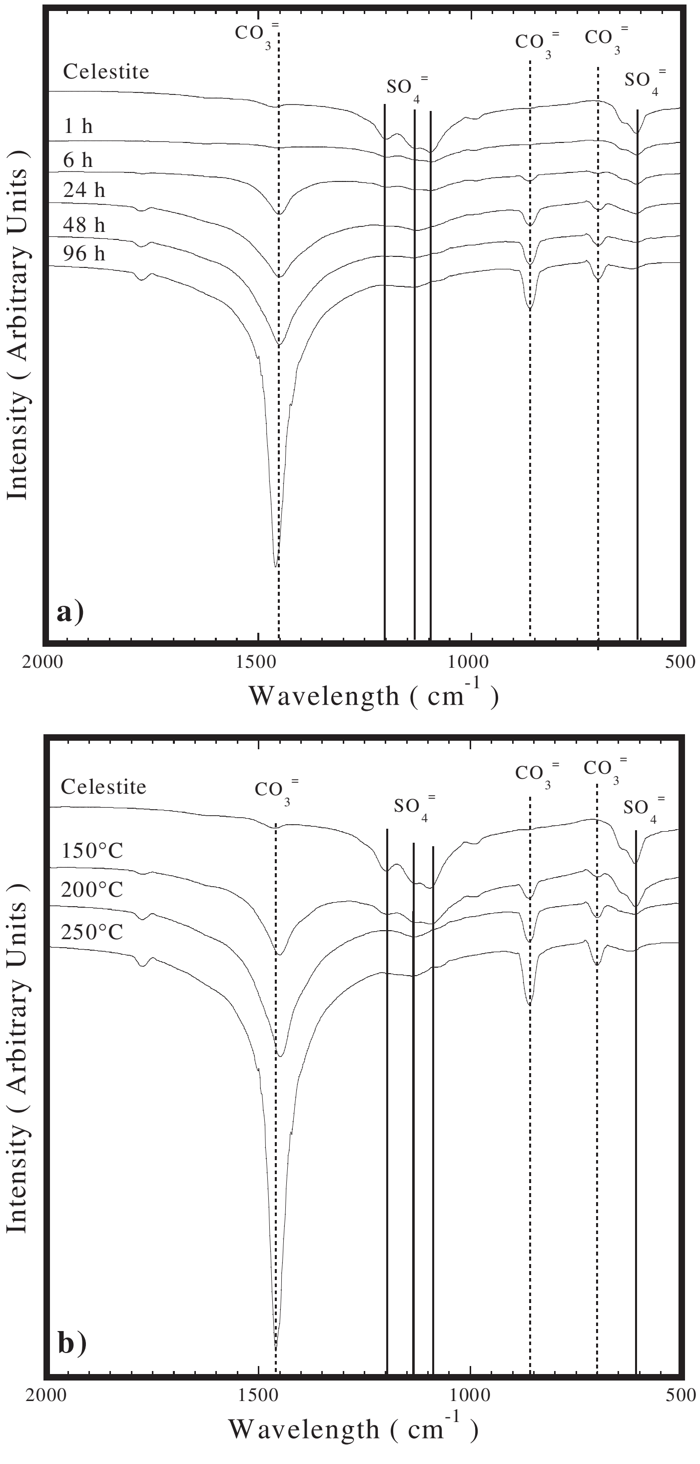

Figure 2. Infrared spectra of the reaction products obtained by hydrothermal treatments in a solution of Na_2CO_3 with a molar ratio CO_3^{2-}/SO_4^{2-} (a) at 250 °C for various reaction times and (b) for 96 h at various temperatures. Dotted lines = CO_3^{2-} vibration bands; solid lines = SO_4^{2-} bending bands.

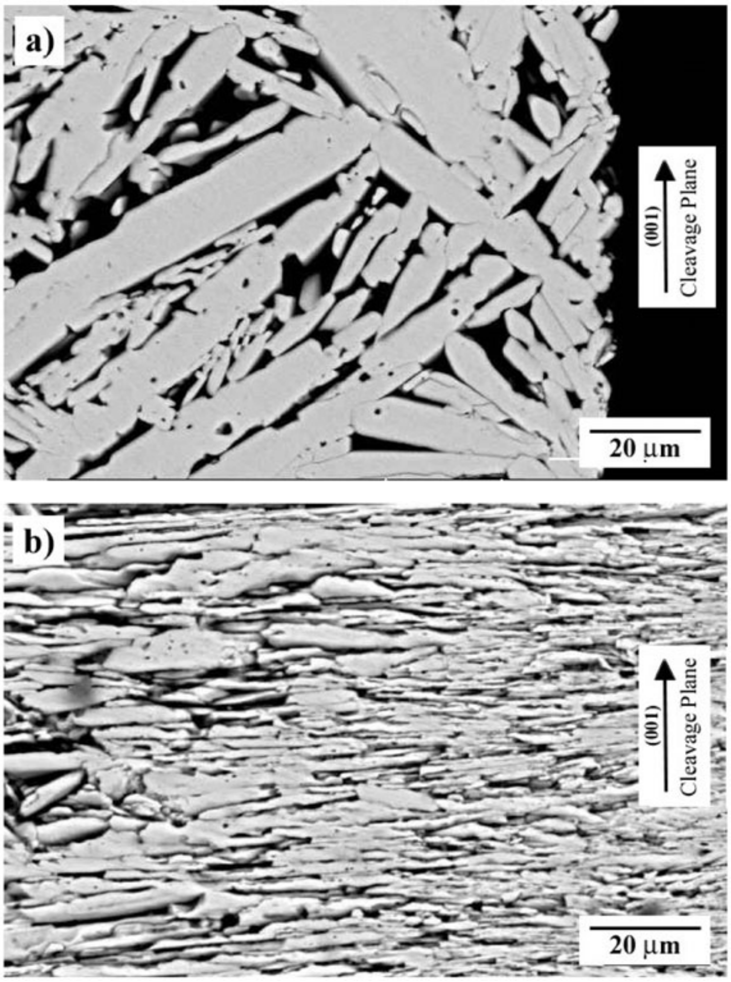

Figure 3. SEM images of a cross section perpendicular to the cleavage plane (001) of a celestite crystal treated at 250 °C in a solution of Na_2CO_3 with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 for (a) 24 h and (b) 96 h.

In general, the hydrothermal treatments in a concentrated Na_2CO_3 solution resulted in reduced transparency of the original crystals, but the transformed strontianite crystals macroscopically retained their original shape and dimensions. It is well known that conventional hydrothermal treatments, especially with a temperature gradient, produce new crystals from the original ones by means of dissolution and precipitation processes [11]. In our investigation, no extra crystals were formed during the treatments. The morphology of the remaining products is shown in figure 3. The SEM images were taken on a polished cross section parallel to the cleavage plane (001) of the crystal. Although the aspect of crystals remained unchanged after the conversion process, some large holes randomly distributed were produced on the layer obtained near the crystal surface during earlier stages of the reaction (figure 3(a)). In contrast, a change of the texture obtained by short reaction times was observed to occur in the exchanged layer, when the crystal was hydrothermally treated for 96 h. Thus, the holes were further reduced in shape and dimensions, and preferentially aligned perpendicular to the cleavage plane (001), as shown in figure 3(b).

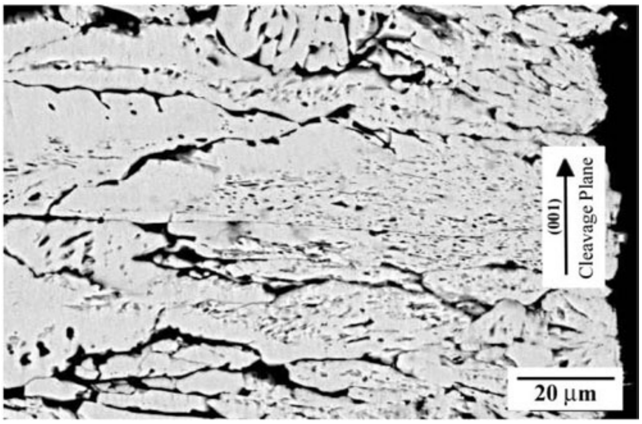

Figure 4. SEM image of a cross section perpendicular to the cleavage plane (001) of a celestite crystal treated at 250 °C in a solution of K_2CO_3 with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 for 24 h.

3.2. Hydrothermal treatments in K_2CO_3 solutions

The crystallographic transformation to strontianite ($SrCO_3$) was also found to occur in celestite single crystals exposed to different alkaline carbonated solutions. The SEM image of a cross section of a partially converted crystal at 250 °C for 24 h using a K_2CO_3 solution with a molar ratio of 10 is shown in figure 4. The crystal treated in the K_2CO_3 solution exhibited fewer corroded surfaces compared with that treated in the Na_2CO_3 solutions. Irregular, randomly distributed cavities, with a width of 0.5–2.5 μm, were also formed on the cross section of the crystal perpendicular to the cleavage plane direction (001). These holes are smaller in size in comparison with the large holes (5–20 μm width) found in the crystal treated at the same conditions in the Na_2CO_3 solution. Yanagisawa *et al* [11] found an anisotropy in these textures, during the conversion of chlorapatite crystals to hydroxyapatite crystals in KOH or NaOH solutions under hydrothermal conditions. Hence, the differences in textures obtained in the crystals might be associated with the dissolution capacity of the celestite in the alkaline ion-exchange media.

3.3. Lattice cell of the hydrothermally converted strontianite crystals

The variation of the lattice cell volume based on the orthorhombic cell was calculated for the converted strontianite phase obtained with various reaction times and temperatures. The results are shown in figure 5 and summarized in table 1. A reduction of the lattice cell volume was observed in the strontianite phase obtained for a short reaction time (1 h) from the original value of celestite (312.37 Å^3). At longer reaction times, no further reduction was observed in the lattice volume of the products, which had values (259.5 Å^3) similar to that of the mineral strontianite (259.06 Å^3). Furthermore, a slight reduction of this parameter was achieved by increasing the reaction temperature above 200 °C (figure 5(b)). In contrast, the products obtained at intermediate stages of the conversion in K_2CO_3 solutions exhibited higher lattice cell volume values than those obtained in Na_2CO_3 solutions. However, a value of 259.13 Å^3, which is near to that of pure mineral strontianite, was achieved in the converted crystal treated for the longest reaction time (96 h).

In general, the values of lattice cell volume determined for the reaction products obtained by treatments conducted for long reaction times (>24 h, figure 5(a)) in both alkaline Na_2CO_3

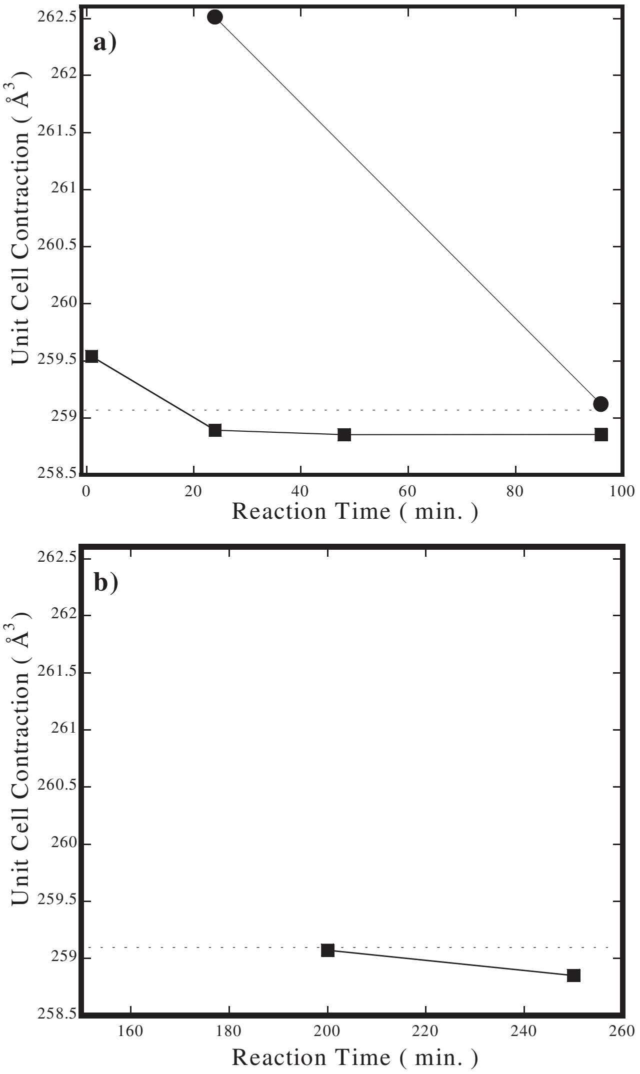

Figure 5. The lattice cell volume variation of converted strontianite crystals, assigned to the orthorhombic system, after hydrothermal treatments (a) in Na_2CO_3 (box) and K_2CO_3 (circle) solutions with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 at 250 °C for various reaction times; (b) in a solution of Na_2CO_3 with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 at different temperatures. Dotted line: volume of the orthorhombic cell of strontianite determined from the lattice parameters in table 1.

or K_2CO_3 solutions are similar to the pure mineral strontianite which may incorporate only a small amount of impurities (Ba <0.1%, Na <0.01%). Though the raw celestite crystals incorporated a large amount of barium (3.83 wt%), the values of the lattice cell volume of the converted strontianite were similar to the pure mineral strontianite, which might be associated with a complete release of the major impurity, Ba, in the raw mineral celestite. The result suggests that the removal of Ba and other impurities proceeds simultaneously during the topotaxial hydrothermal conversion. This inference is supported by the fact that energy dispersive x-ray analyses did not exhibit any traces of impurities (Ba and Ca) in the completely converted strontianite crystals. The purification of a mineral species is a common process that is achieved under hydrothermal conditions, when the mineral is simultaneously dissolved and recrystallized.

When the cell volume values of the converted strontianite obtained by the treatment for a short time (24 h) were compared, the Na_2CO_3 solution gave a smaller value than the K_2CO_3 solution. This result shows that the hydrothermal treatments in Na_2CO_3 solution result in a purer strontianite, rather than in K_2CO_3 solutions. Dissolution of celestite has been reported to occur in concentrated Na_2CO_3 solutions over a large range of pH (5–10) at 80 °C in air [5]. Though the data on dissolution of celestite in K_2CO_3 solutions have not been reported yet, the difference might be explained by the lower dissolution capability of celestite in K_2CO_3 solutions in which the conversion rate and the release of the impurities were slightly reduced.

3.4. Characterization of texture and structure of the hydrothermal ion-exchanged products

We have found that the conversion of celestite to strontianite proceeds at low temperatures in alkaline hydrothermal conditions (Na_2CO_3 or K_2CO_3 solutions), with the formation of a peculiar texture on the surface and inside the converted strontianite crystals. The development of this texture may be explained as follows.

The dissolution of mineral species in hydrothermal fluids normally proceeds anisotropically, producing a peculiar texture with holes inside the recrystallized mineral specie [11, 12]. The holes might not be inherited from etch pits produced during dissolution, because they did not penetrate the crystals. The peculiar texture, consisting of elongated holes randomly distributed parallel to the *b* axis of the orthorhombic structure, can be attributed to the changes of the celestite structure by the replacement of large ions ($SO_4^{2-} = 4.320$ Å) by small ions ($CO_3^{2-} = 1.550$ Å). In terms of the lattice parameter, two processes are involved: a contraction of 3.258 and 0.838 Å along the *a* and *c* axis of the orthorhombic structure, respectively, and an expansion of 3.062 Å along the *b* axis. Therefore, in accordance with the differences in the unit cell volume between celestite (307.06 $Å^3$) and strontianite (259.07 $Å^3$), a global unit cell volume contraction of 47.99 $Å^3$ must occur as a result of the ion-exchange reaction. Hence, the volumetric unit cell contraction must be compensated for, which is achieved by the formation of holes inside the partially and completely converted strontianite crystals.

3.5. Characteristics of the mechanism for carbonate ion exchange under hydrothermal conditions

Details of the course of the ion-exchange mechanism were investigated by observing the cross section of the partially ion-exchanged crystals obtained by hydrothermal treatment at 250 °C for 1 h with a molar ratio $CO_3^{2-}/SO_4^{2-} = 10$. Figure 6 shows an SEM image taken of the cross section of a crystal normal to the cleavage plane (001). In the SEM photograph, it is easy to identify two phases: a porous phase near the crystal surface, and a continuous part inside the crystal which corresponds to original celestite. It is interesting to note that the outer layer developed at this stage contains holes that are distributed randomly normal to the cleavage basal plane (001). The phases are separated by a sharp boundary in texture. From these observations it is clear that the ion exchange begins from the surfaces of the crystal that were in contact with the reaction fluid. In addition, the reaction proceeds by the penetration of the reaction media through the holes that trace a zigzag course inside the crystal [11, 14].

Hitherto, it has been reported that the exchange of SO_4^{2-} by CO_3^{2-} can proceed by a topochemical process [5, 6]. This process was proposed to lead the conversion of celestite particles (approximated grain size of 50 μm) in a concentrated Na_2CO_3 solution at 80 °C. Under these conditions, a mechanism of topotactic dissolution of the particles achieves the formation of an

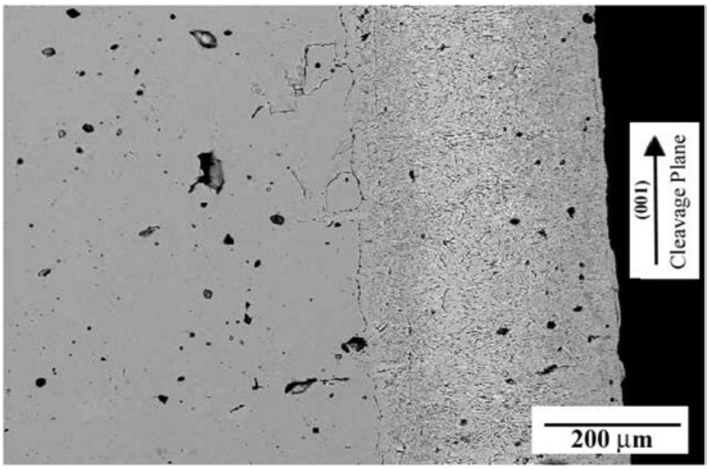

Figure 6. SEM image of a cross section of a partially converted celestite crystal normal to the cleavage plane (001), obtained by hydrothermal treatment in a Na_2CO_3 solution with a molar ratio $CO_3^{2-}/SO_4^{2-} = 10$ at 250 °C for 1 h.

$SrCO_3$ layer on the surface of the celestite particles, and the conversion is completed due to the diffusion of SO_4^{2-} ions through the porous $SrCO_3$ layer. A different mechanism for the ion exchange of SO_4^{2-} with CO_3^{2-} between celestite crystals and whiterite ($BaCO_3$) powder [7] was proposed to proceed in solid state conditions even under hydrothermal conditions at 500 °C for 168 h at high pressure (100 MPa). It was found that an atomic diffusion mechanism achieved the anion motion through the crystalline structure of celestite and whiterite crystalline phases. It is well known that at solid state conditions, the crystalline structure and the crystalline defects play important roles for ion exchange, because the motion of ions may be accelerated by the interaction between vacancies and ions [11, 14]. The conversion investigated in the present work, however, cannot be associated with a solid state ion exchange, because it proceeded at low temperatures in comparison with that necessary to achieve atomic diffusion in the solid state [7].

Observations with high magnification conducted near the reaction interface on partially reacted celestite crystal showed that the reacted layer consists of two parts (figure 7(a)). A sulfur x-ray line profile over the distance between the arrows in figure 7(a) was taken in the direction in which the conversion proceeded normal to the plane (001) of the orthorhombic structure. The profile (figure 7(b)) reveals that two sharp boundaries in the sulfur composition are formed in the reaction interface. Three different parts are delimited by the sharp concentration boundaries: a highly reacted part near the surface of the crystal with a lowest sulfur content and a great number of holes randomly distributed, an intermediate layer (chemical composition determined by WDX $Sr(CO_3)_{0.73}(SO_4)_{0.27}$, using mineral celestite as a standard) of approximately 15 μm thick with a small amount of sulfur and very tiny holes, and the unreacted celestite part with high sulfur content and smooth surface. Thus, the conversion of celestite crystals to strontianite crystals proceeded with a preferential formation of a series of CO_3^{2-}-rich solid solutions in the system $SrCO_3$–$SrSO_4$ at the reaction interface. We consider that the formation of the solid solutions and the bulk conversion of celestite to strontianite under alkaline hydrothermal conditions proceed by the mechanism of dissolution precipitation of clusters [11]. In addition, these results are in good agreement with the reaction trend that was found to occur during the topotaxial conversion of Sr-chlorapatite to Sr-hydroxyapatite under

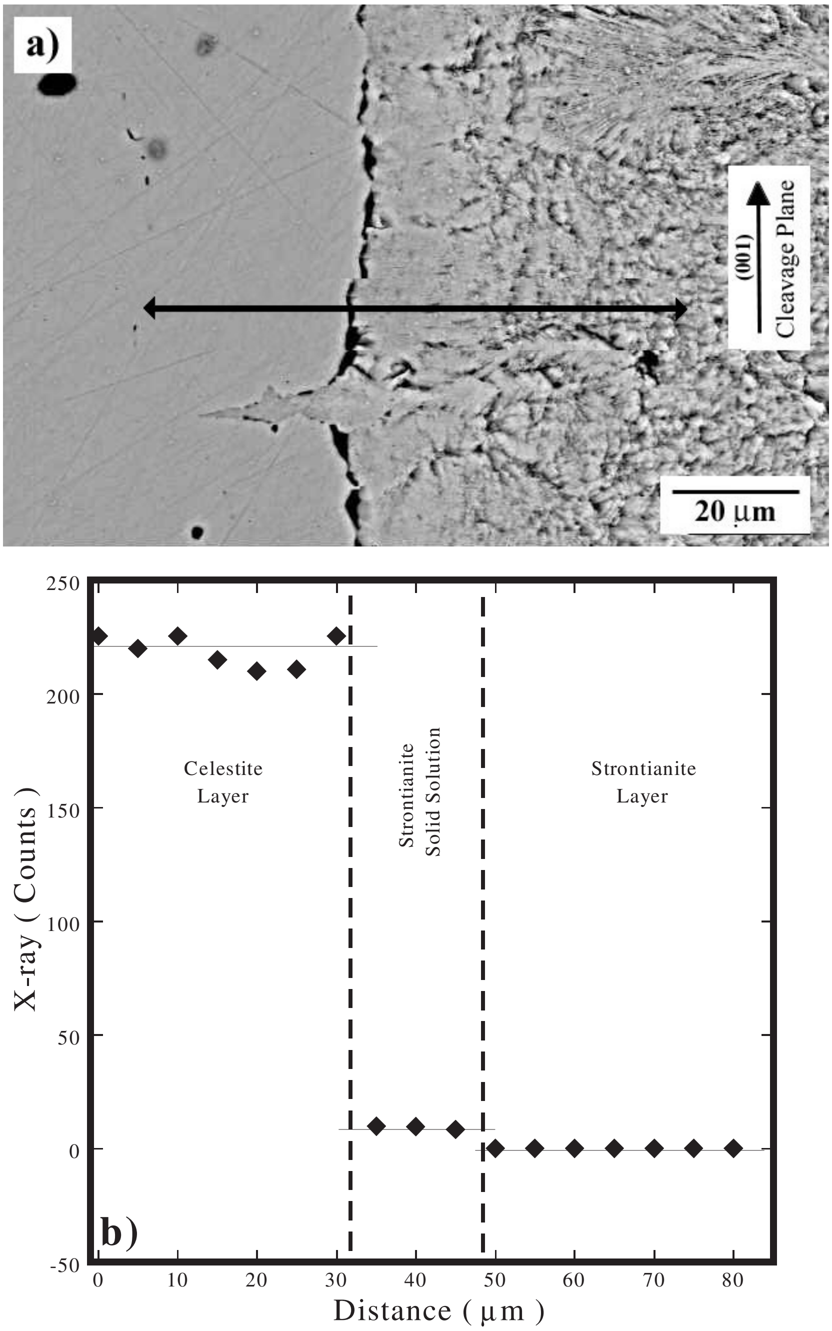

Figure 7. (a) SEM image of the reaction interface and (b) sulfur concentration in a partially converted celestite crystal obtained by hydrothermal treatment in a Na_2CO_3 solution with a molar ratio $CO_3^{2-}/SO_4^{2-} = 10$, at 250 °C for 1 h.

alkaline hydrothermal conditions [12]. After the topotaxial conversion, the solid solutions underwent further dissolution and precipitation to form a highly reacted part near the surface of the crystal.

4. Conclusions

Mineral celestite single crystals ($SrSO_4$, square plates 10 mm wide and 3 mm thick) were topotaxially converted to strontianite ($SrCO_3$) under alkaline hydrothermal conditions. The reaction was completed in a short reaction time (such as 1 h) at a temperature of 250 °C. The exchange of SO_4^{2-} ions with CO_3^{2-} ions was accelerated by increasing the treatment temperature and molar ratio CO_3^{2-}/SO_4^{2-}. It was found that the topotaxial hydrothermal conversion to strontianite proceeds with the formation of intermediate CO_3^{2-}-rich solid solutions in the system $SrCO_3$–$SrSO_4$, and these solid solutions were formed by the dissolution–recrystallization mechanism of clusters. An anisotropic dissolution gave a characteristic texture in the converted crystals, and the difference in the reactivity of the celestite crystals in Na_2CO_3 and K_2CO_3 solutions resulted in a different textures inside the topotaxially converted strontianite crystals.

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