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Stability and direct conversion of mineral barite crystals in carbonated hydrothermal fluids

J. C. Rendón-Angeles · Z. Matamoros-Veloza ·
J. López-Cuevas · M. I. Pech-Canul ·
K. Yanagisawa

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Abstract The pseudomorphic replacement of mineral barite ($BaSO_4$) crystals into barium carbonate was investigated in the present work by using carbonated alkaline hydrothermal fluids. Hydrothermal treatments were carried out over the temperature range from 150 up to 250 °C for intervals between 1 and 192 h, with different filling ratios (40–70%), and CO_3^{2-}/SO_4^{2-} molar ratios of 1, 5, and 10. The reaction products were characterized by XRD and SEM techniques. The chemical reactivity of mineral barite crystals was markedly limited at temperatures below 200 °C, and only a tiny $BaCO_3$ layer on the surface of the original $BaSO_4$ crystal was formed on the crystal treated for 192 h. The rate of the pseudomorphic conversion of $BaSO_4$ into $BaCO_3$, was accelerated by increasing the reaction temperature and the molar ratio CO_3^{2-}/SO_4^{2-}. Powder X-ray diffraction results showed that under hydrothermal conditions the replacement of SO_4^{2-} ions by CO_3^{2-} ions, in barite crystals was completed at 250 °C with a molar ratio $CO_3^{2-}/SO_4^{2-} = 10$ for an interval of 192 h, resulting in the Witherite structure. The morphology of the completely converted $BaCO_3$ at 250 °C in a Na_2CO_3 solution for 192 h, showed that the conversion proceed without severe changes of the original shape and dimension of the original crystal, similar to that observed in mineral pseudomorphic replacement process.

Introduction

Hitherto, the anionic replacement of SO_4^{2-} ions with CO_3^{2-} in mineral barite specie has not been properly studied. This particular reaction is important due to the chemical and structural similarities that the mineral barite specie ($BaSO_4$) has with other related alkaline earth sulfate; such as the celestite ($SrSO_4$) [1]. Furthermore, the mineral barite specie is the main raw source for preparing barium inorganic compounds [2]. The ionic mineral replacement reactions have widely been investigated because these occur in hydrothermal ore deposits. These typical chemical reactions are mainly achieved by a mechanism of dissolution-recrystallization [3].

The first evidences on the replacement of SO_4^{2-} ions with CO_3^{2-} ions were reported by Iwai et al.[4], who studied the leaching of strontium sulfate ($SrSO_4$, mineral celestite) from a thermodynamic and kinetic point of view. They reported that in large bulk $SrSO_4$ crystals plates the replacement of SO_4^{2-} ions by CO_3^{2-} ions is achieved in two different steps. The initial reaction occurs at the crystal surface where a thin solid $SrCO_3$ layer is precipitated. The second mechanism proposed is related with SO_4^{2-} ion motion through the dense $SrCO_3$ layer. Moreover, other researchers have reported that during the leaching reaction of celestite particles, the conversion of $SrSO_4$ to $SrCO_3$ is mainly achieved by a topochemical mechanism [5]. However, in all the above cited references, details on the effect of the crystallographic structural changes associated with

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J. C. Rendón-Angeles (✉) · J. López-Cuevas ·
M. I. Pech-Canul
Research Center for Advanced Studies of the NPI,
Campus-Saltillo, Carr. Saltillo-Mty Km. 13.5, Col. Molinos del
Rey, Ramos Arizpe 25900 Coahuila, Mexico
e-mail: jcarlos.rendon@cinvestav.edu.mx

Z. Matamoros-Veloza
Department of Metal-Mecánica, Saltillo Institute of Technology,
Saltillo, Coahuila 25820, Mexico

K. Yanagisawa
Research Laboratory of Hydrothermal Chemistry,
Kochi University, Kochi 780-8520, Japan

the conversion were discussed. Furthermore, Yoshino et al. [6] have found the first evidences that demonstrate, even under hydrothermal conditions at pressures between 1 and 100 MPa, the replacement of SO_4^{2-} ions with CO_3^{2-} ions is achieved by a solid state atomic diffusion. During the anion replacement, the reaction interface of the celestite crystal remains without remarkable morphological variation, and bears a SO_4^{2-} concentration gradient across it. This fact was also confirmed by Brenan [7], who determined the influence of pressure on the diffusion coefficients of several anions in mineral apatite during hydrothermal treatments.

Recently, the present authors have found that a different replacement mechanism is involved in the conversion of a related mineral alkaline earth ($SrSO_4$, Celestite) into $SrCO_3$ in carbonated hydrothermal fluids [8]. The anion replacement of SO_4^{2-} ions with CO_3^{2-} ions in the natural $SrSO_4$ mineral specie was carried out at different temperatures from 150 to 250 °C for various reaction intervals (1–96 h) and SO_4^{2-}/CO_3^{2-} molar ratios of 1, 5, and 10. It was found that the SO_4^{2-} replacement in Celestite crystals by CO_3^{2-} ions completely occurred at very low temperature (250 °C) in a Na_2CO_3 solution with a CO_3^{2-}/SO_4^{2-} molar ratio of 10 for 96 h. After the hydrothermal treatment, it was observed that the bulk morphology of the $SrCO_3$ converted crystal was nearly similar to that of the original mineral $SrSO_4$ crystal. However, the formation of a peculiar texture consisting by tiny tunnels randomly distributed inside the converted crystal occurred as a consequence of the anion replacement reaction [8]. The presence of this particular texture is likely to proceed in order to compensate the volume molar changes due to the replacement of large ions (SO_4^{2-} = 4.32 Å) with smaller ions (CO_3^{2-} = 1.55 Å). This particular conversion was associated with the pseudomorphic replacement process, which is mainly achieved by a coupled dissolution-precipitation mechanism [3, 8].

A wide variability exists in the replacement reaction mechanism that proceeds in some related alkaline earth sulfate minerals, even in hydrothermal conditions. Furthermore, from the scientific point of view, this particular way of conversion is an emerging processing technique for the preparation of quasi net-shaped inorganic compounds and ceramic materials. Thus, much research work must be carried out in order to elucidate all the aspects related with the reaction mechanisms by which a pseudomorphic reaction occurs [3]. Hence, in the present research work, we attempted to determine the chemical stability of mineral barite crystals ($BaSO_4$) under hydrothermal conditions by using concentrated carbonate solutions. Furthermore, the feasibility to replace the SO_4^{2-} ions with CO_3^{2-} ions in the structure of the crystals was also investigated. Initial attempts were made in order to determine the differences in the conversion of barite ($BaSO_4$) to $BaCO_3$ by using two different carbonated solutions of Na_2CO_3 and K_2CO_3.

Experimental procedure

Materials

Barite mineral crystals were obtained from typical mineral ores placed at the northwestern of Mexico (Coahuila). The raw mineral was cut at a direction parallel to the cleavage plane (001) of the crystals by using a diamond blade, in order to obtain 10 mm wide and 3 mm thick squared plates, the length of the crystal was determined by the total weight of $BaSO_4$ needed to keep the desired value of the molar CO_3^{2-}/SO_4^{2-} ratio. These plates were washed with deionized water and cleaned by employing ultrasonic equipment. Preliminary X-ray powder diffraction analyzes demonstrate that the structure of the barite crystals corresponds to the orthorhombic system (space group *Pbnm*), and the unit cell dimensions are as follows: a = 7.1560 0.0004 Å, b = 8.8805 ± 0.0004 Å, and c = 5.4521 0.0004 Å. Reagent grade Na_2CO_3 and K_2CO_3 (Aldrich) were used such as hydrothermal fluid media.

Hydrothermal treatments

Three different molar CO_3^{2-}/SO_4^{2-} ratios of 1, 5, and 10, which correspond to concentrations of 0.28, 1.43, and 2.87 M for both Na_2CO_3 and K_2CO_3 solutions, respectively, were used as reaction media. For each run, the plate of single crystal of Barite ($BaSO_4$) was placed at the Teflon-lined stainless steel vessel; the fill ratio was varied from 40 to 70% to obtain an internal pressure from 20 to 100 MPa for the hydrothermal treatments. The vessel was heated to a predetermined temperature (150–250 °C) with a heating ratio of 10 °C/min. After being held at each temperature for several hours (1–192 h), the vessel was removed from the oven and then cooled to room temperature by means of an electric fan. After the hydrothermal treatment, the vessel was open, and the content was washed with deionized distilled water. The obtained samples were cleaned by means of ultrasonic equipment. For a few experiments, the weight loss caused by dissolution was measured.

Characterization

Powder X-ray diffraction analyses were employed to determine the crystalline phases and the lattice constants of the treated crystals. Measurements were made on a Philips 3040 X-ray diffractometer with CuKα radiation at 40 kV and 100 mA. Diffraction patterns were taken of the 2θ range from 10 to 80° 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 from 35 to 55 at a scanning speed of 0.2°/min and step sampling interval of 0.006°, using Si as an internal standard. Moreover, morphological aspects of the crystals and details on the replacement reaction were examined by scanning electron microscopy (Philips XL30 ESEM). In addition, sulfur line scanning analyses were conducted by means of an energy dispersive X-ray device. The surface observed was perpendicular to the cleavage plane (001) of the crystals.

Results and discussion

The experiments for the conversion of barite to barium carbonate under hydrothermal conditions were directed toward for evaluating the effect of the following factors: temperature, reaction interval, and the molar ratio $CO_3^{2-}/SO_4^{2-}$of the reaction media. In Table 1 are summarized the most relevant results related with the conversion of $BaSO_4$ crystals to $BaCO_3$ polycrystals, Table 1 also includes the experimental conditions and the crystalline phases obtained on the reaction products. In the reaction products, one point that deserves emphasis is that related with the experiments conducted with a molar CO_3^{2-}/SO_4^{2-} ratio of 1 or 5. In particular, in both cases the hydrothermal conversion was further limited at temperatures and reaction intervals below 250 °C and 96 h, at these conditions the formation of the reaction layer was not detected after the treatment, though few experiments conducted at these molar ratios are included in Table 1. Therefore, a particular attention was directed to analyze the conversion reaction at a molar CO_3^{2-}/SO_4^{2-} ratio of 10, these results are described as follows.

Hydrothermal treatments of barite crystals in Na_2CO_3 and K_2CO_3 alkaline solutions

The results of the structural changes that occurred on barite crystals were revealed by the X-ray diffraction patterns shown in Fig. 1a. The barite crystal plates were hydrothermally treated at various temperatures for 192 h, in a Na_2CO_3 solution with a molar ratio of $CO_3^{2-}/SO_4^{2-}$of 10. These results revealed that the replacement of SO_4^{2-} ions by CO_3^{2-} ions in the crystals began at temperatures as low as 150 °C. At this temperature, a small amount of a new secondary crystalline phase was obtained in the reaction products, and the amount of this phase was progressively increased at higher reaction temperatures. Thus, when the barite crystals were treated at 250 °C, the new single phase was found to be the only constituent present on the reaction products. This new single phase was indexed with that of the whiterite ($BaCO_3$) orthorhombic structure (space group *Pmcn*, JCPDS card 05–0378). These results indicate that the direct conversion of mineral barite crystals to $BaCO_3$ under alkaline hydrothermal conditions was gradually accelerated by increasing the reaction temperature.

Furthermore, in Fig. 1b are shown the diffraction patterns of the crystals treated at 250 °C with a Na_2CO_3 solution with a molar ratio $CO_3^{2-}/SO_4^{2-}$of 10 and a 70% filling ratio, for several reaction intervals. From these results, it was found that the formation of the $BaCO_3$ phase in the barite crystals occurred for reaction intervals as short as 24 h. The increase in the reaction interval up to 192 h, as in the case of the temperature; resulted in the complete transformation of the barite to $BaCO_3$ (like witherite structure). Thus, at this reaction interval the $BaSO_4$ crystals were completely converted into $BaCO_3$. In addition, a similar reaction trend as that determined for other experimental parameters, namely the temperature and reaction interval, was found in the case of the variation of concentration of the solvent solution (molar ratio CO_3^{2-}/SO_4^{2-}). The amount of $BaCO_3$ on the reaction products was gradually increased by increasing the molar ratio CO_3^{2-}/SO_4^{2-}up to a value of 10 (Fig. 1c). In general, the $BaCO_3$ diffraction peaks have a slightly shifting to higher angle, in comparison with the peaks location of the witherite structure. The shifting is marked in the specimens treated during early and intermediate stages of treatment. In particular, this phenomenon could be associated with the formation of solid solution in the binary system $BaCO_3$–$BaSO_4$, because this is a particular replacement reaction pattern that was even found to proceed in other related sulfate minerals such as celestite ($SrSO_4$) [8, 9].

Microstructural aspects of the converted $BaCO_3$ crystals

The hydrothermal treatments in a concentrated Na_2CO_3 solution resulted in reduced transparency of the original crystals, but the converted barite crystals macroscopically retained their original morphology, regarding their shape and dimensions. In conventional hydrothermal treatments, especially with a temperature gradient, new crystals are produced from the original by means of dissolution and precipitation process [10]. In our particular case, the treatments in the concentrated Na_2CO_3 or K_2CO_3 solutions transformed the barite crystals to barium carbonate, but the formation of crystalline secondary phases did not occur.

Details on the morphology of the remaining reaction products are shown in Fig. 2. The SEM micrographs correspond to a polished cross section parallel to crystal surface. Although the aspect of crystals remained without any change after the conversion process, some large holes

Table 1 Summary of hydrothermal treatments of barite single crystals in carbonated solutions

Sample ID	Mineralizer	Molar ratio CO_3^{2-}/SO_4^{2-}	Temperature (°C)	Time (h)	Fill ratio (%)	Crystalline phases	Lattice parameters			Volume cell (Å^3)
							a(Å)	*b*(Å)	*c*(Å)	
Ba1	Na_2CO_3	10	250	24	70	$BaSO_4$ + SS-$BaCO_3$*	5.293	8.825	6.409	299.369
Ba3	Na_2CO_3	10	250	48	70	$BaSO_4$ + SS-$BaCO_3$*	5.297	8.854	6.414	300.814
Ba4	Na_2CO_3	10	250	96	70	$BaSO_4$ + SS-$BaCO_3$*	5.304	8.867	6.423	302.077
Ba6	Na_2CO_3	10	250	192	70	$BaCO_3$*	5.311	8.895	6.428	303.667
Ba9	Na_2CO_3	10	250	192	55	$BaCO_3$*	5.303	8.893	6.427	303.094
Ba10	Na_2CO_3	10	250	192	40	$BaSO_4$ + SS-$BaCO_3$*	5.312	8.890	6.424	303.364
Ba12	Na_2CO_3	1	250	192	70	$BaSO_4$ + SS-$BaCO_3$**	–	–	–	–
Ba15	Na_2CO_3	5	250	192	70	$BaSO_4$ + SS-$BaCO_3$*	5.290	8.810	6.398	298.17
Ba7	Na_2CO_3	10	200	192	70	$BaCO_3$*	5.300	8.865	6.428	302.016
Ba8	Na_2CO_3	10	150	192	70	$BaSO_4$ + SS-$BaCO_3$**	–	–	–	–
Ba13	K_2CO_3	10	250	192	70	$BaCO_3$*	5.312	8.897	6.427	303.745
Ba14	K_2CO_3	10	250	96	70	$BaSO_4$ + SS-$BaCO_3$*	5.307	8.879	6.428	302.892
Barite ($BaSO_4$ raw material JCPDS card 24–1,035)							7.156	8.8805	5.452	346.468
Witherite ($BaCO_3$ raw mineral JCPDS card 05–0378)							5.314	8.904	6.430	304.240

Note: *The lattice parameters were calculated for the converted either SS-$BaCO_3$* or $BaCO_3$*

**The lattice parameter of the major reaction product SS-$BaCO_3$ was not calculated because at these experimental conditions, sufficient amount of this product could not be collected from the partially reacted $BaSO_4$ crystal in order to perform the X-ray analyses

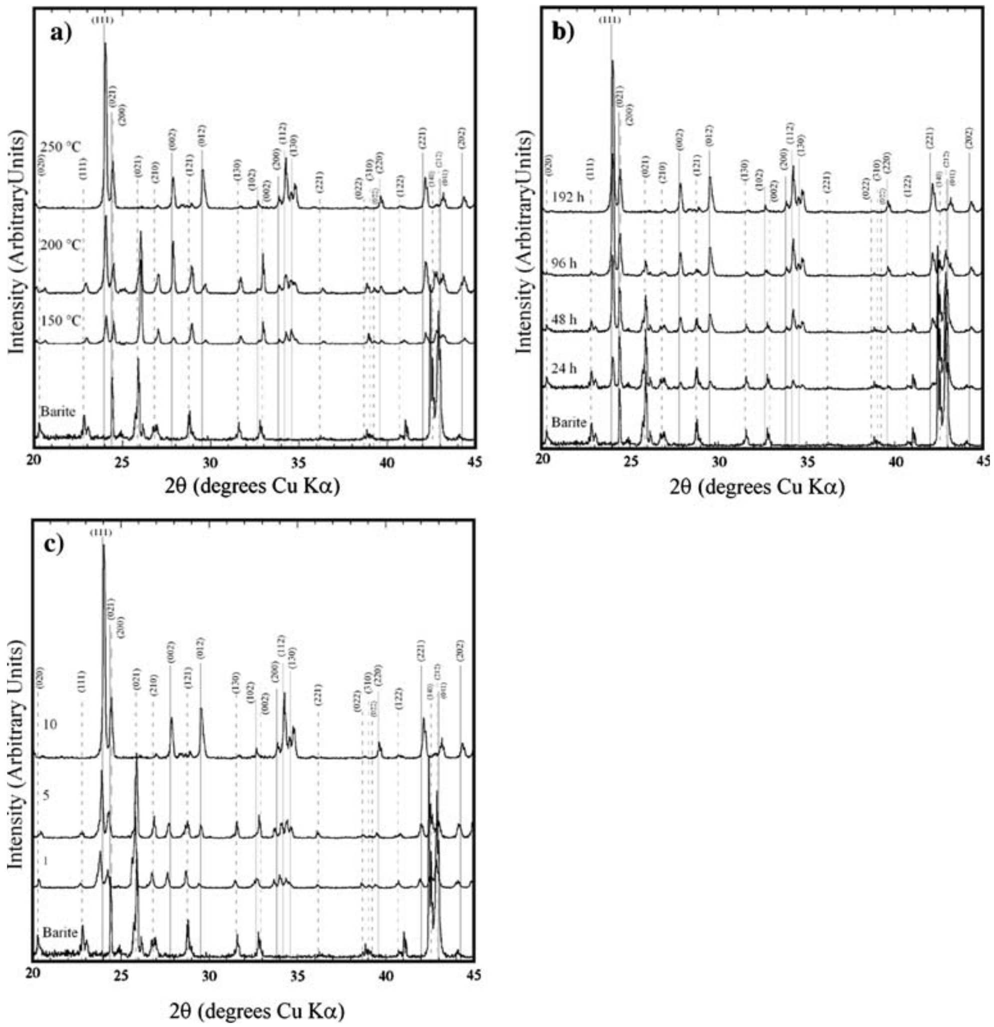

Fig. 1 XRD patterns of the specimens obtained from barite crystals after hydrothermal treatments using a Na_2CO_3 solution with a molar ratio CO_3^{2-}/SO_4^{2-} of 10, (**a**) for 192 h at several temperatures, (**b**) at a temperature of 250 °C for several time intervals and (**c**) at a temperature of 250 °C for 192 h with different molar ratios

randomly distributed were produced on the layer obtained near the crystal surface during earlier stages of the reaction (Fig. 2a). In contrast, a change of the texture obtained by short reaction intervals was observed to occur in the layer produced at the crystals surface, when the mineral crystal was hydrothermally treated for 192 h. However, there are some zones in the new converted layer near the reaction front that indicate the $BaCO_3$ layer underwent a significant dissolution in the carbonated hydrothermal solution. In addition, it was found that the crystallographic conversion of $BaSO_4$ into $BaCO_3$ was also found to proceed in the barite single crystals treated with a different alkaline solution, K_2CO_3.

Figure 3 shows the microstructural differences of completely converted barium carbonate crystal under hydrothermal conditions at 250 °C for a reaction interval of 192 h, in two different alkaline solvent media, Na_2CO_3 or K_2CO_3, with a molar ratio CO_3^{2-}/SO_4^{2-} of 10. In general, it was found that the peculiar microstructure of the $BaCO_3$ crystals converted in highly concentrated carbonated solutions is irrespective of the type of carbonated alkaline media, Na_2CO_3 or K_2CO_3, because in both cases a great number of holes randomly distributed inside the converted crystals were formed, Fig. 3. However, the crystal converted in the K_2CO_3 solution exhibited fewer corroded zones compared with that revealed in the crystal treated in Na_2CO_3 solution. A great amount of irregular randomly distributed cavities, with a width of 5–40 μm, were formed inside the crystal. These cavities are larger than the holes (1–10 μm) found in the crystal treated in K_2CO_3 solution. The texture anisotropy found in the converted $BaCO_3$ crystals might be explained by the chemical reaction capacity of the raw mineral and converted phase with the carbonated alkaline media [9]. Additional details of the

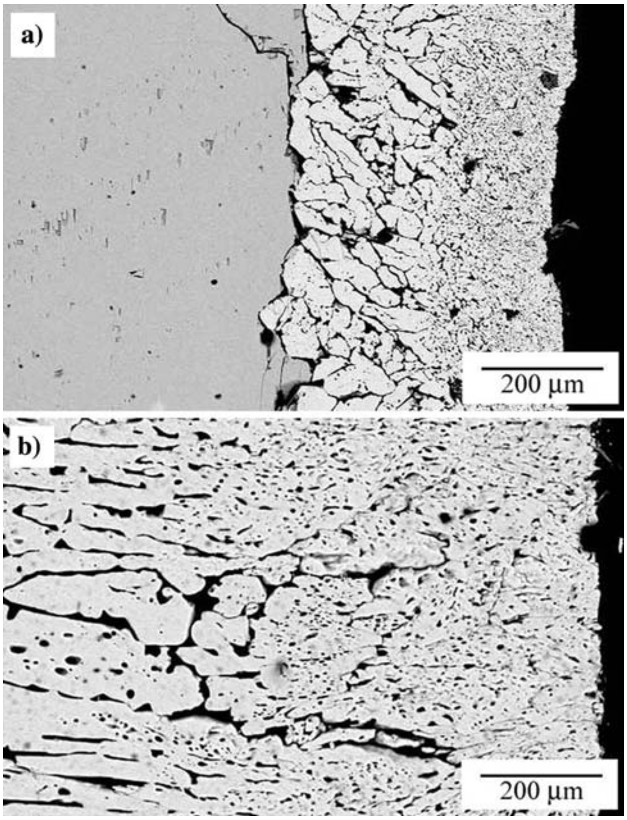

Fig. 2 SEM micrographs of barite crystals converted to barium carbonate after hydrothermal treatment at 250 °C in a Na_2CO_3 solution with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 for different reaction intervals (**a**) 24 h (**b**) 192 h

conversion reaction were determined by energy dispersive X-Ray area analyses, which were conducted on the cross section of the complete hydrothermally converted $BaCO_3$ specimens. These analyses depicted that the incorporation of Na^+ or K^+ is not likely to proceed during the conversion process under hydrothermal conditions, because the incorporation of even traces of them was not detected inside the converted specimens.

Volume lattice cell of the hydrothermally converted $BaCO_3$ crystals

The variation of the lattice cell volume based on the orthorhombic cell was calculated for the converted witherite phase obtained with several reaction times and temperatures. The results are shown in Fig. 4 and summarized in Table 1. A marked reduction of the lattice cell volume was observed in the $BaCO_3$ specimen obtained for a reaction interval of 24 h in comparison with the original value of barite (346.47 Å^3). At longer reaction times, no further reduction was observed in the lattice cell volume of the products, which had values of approximately 303.66 Å^3 (Fig. 4a). This value is nearly similar to that of the mineral witherite (304.24 Å^3). Furthermore, a slight reduction of the lattice volume cell was achieved by increasing the reaction temperature above 200 °C (Fig. 4b). In contrast, the products obtained at intermediate stages of the conversion in K_2CO_3 solutions exhibited similar lattice cell volume values that those obtained in Na_2CO_3 solutions.

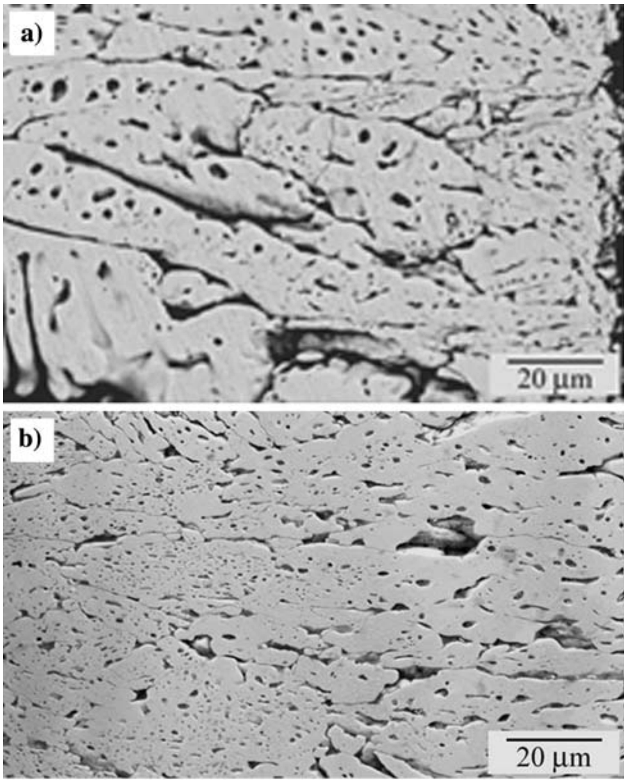

Fig. 3 SEM images of the cross sections of barite crystals converted to barium carbonate at 250 °C for 192 h in two different solvents, (**a**) Na_2CO_3, (**b**) K_2CO_3; with a molar ratio CO_3^{2-}/SO_4^{2-} of 10

We found that the conversion of barite to barium carbonate proceeds at lower temperature under alkaline hydrothermal conditions. In addition, the $BaCO_3$ crystals converted from the barite crystals under hydrothermal conditions had a characteristic texture on their surfaces and inside. The cavities and channels randomly distributed were formed on the surface and inside of the converted $BaCO_3$ crystals, respectively.

These channels are formed by the replacement which proceeds under hydrothermal conditions. In terms of the crystalline structure, the conversion is carried out by the release of large SO_4^{2-} ions having a radius of 4.32 Å, and the incorporation of smaller CO_3^{2-} ions with a radius of 1.55 Å. As a result, the conversion of barite (JCPDS card 24–1035) to witherite (JCPDS card 05–0378) is accompanied by a large contraction along the *a* axis of

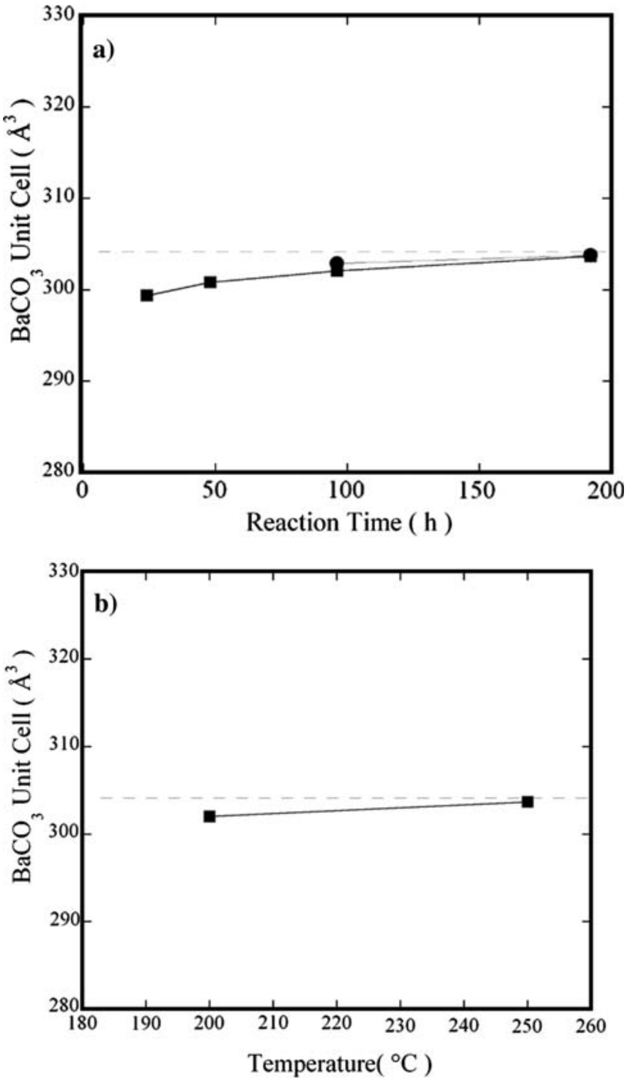

Fig. 4 Variation of the lattice cell volume of converted $BaCO_3$ crystals, after hydrothermal treatments with (**a**) Na_2CO_3 (■) and (●) K_2CO_3 solutions with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 at 250 °C for various reaction times; (**b**) using a Na_2CO_3 solution with a molar ratio CO_3^{2-}/SO_4^{2-} of 10 for 192 h at different temperatures. Dotted line: volume of the witherite orthorhombic cell determined from the lattice parameters in Table 1

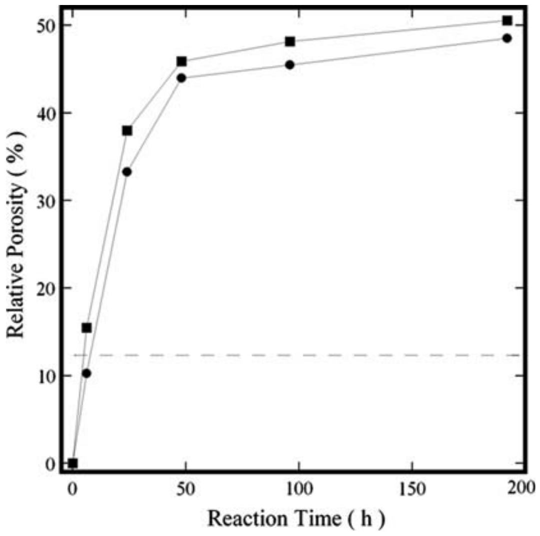

Fig. 5 Variation of the relative porosity measured by using helium picnometry on $BaCO_3$ crystals treated at 250 °C for different reaction intervals in two different solvents (●) Na_2CO_3, (■) K_2CO_3

approximately 26%, and a expansion along the *b* and *c* axis (0.03 and 15%). Thus, in order to maintain the crystal macrostructure, the dimensional change must be compensated for, which appears to proceeds the formation of holes inside the converted $BaCO_3$ crystals. However, the residual porosity in the completely converted crystals seems to be greater than the porosity associated with the structural volumetric contraction above described. Details regarding the level of porosity in partially and completely converted $BaCO_3$ crystals were reveled by helium picnometry analyses. The Fig. 5 shows the variation of porosity determined on partial and completely converted $BaCO_3$ crystals at 250 °C in different mineralizers for several reaction intervals. The discontinuous line drawn on Fig. 5 corresponds to the theoretical porosity value (12%) that is associated with the crystalline transformation of $BaSO_4$ into $BaCO_3$. A significant increase on the residual porosity occurred on the partial and completely converted $BaCO_3$ crystals by increasing the reaction interval. The maximum value of the residual porosity determined on the completely converted specimens for 192 h was 50%. Thus the excess on porosity obtained in the converted crystals above 48 h of treatment, it may be attributed to a bulk dissolution process of the $BaCO_3$ phase Hence, the 38% of the porosity is produced by the dissolution of the barium carbonate, this compound has a low chemical stability under alkaline conditions, which results in achieving the hydrolysis of the Ba^{2+} ions [11]. Hence, the present results depicts that for this particular conversion, the texture produced is due to the bulk volume molar reduction and the further dissolution of the converted phase in the hydrothermal solvent.

Characteristics of the conversion process of $BaSO_4$ into $BaCO_3$ under hydrothermal conditions

The details regarding the replacement process in barite crystals were investigated by observing the cross sections of the partially ion exchanged crystals obtained by hydrothermal treatments in different solutions. SEM photographs of the partially reacted samples after the hydrothermal treatment in the Na_2CO_3 solutions at 250 °C for a interval of 24 h, a fill ratio of 70% and a molar ratio CO_3^{2-}/SO_4^{2-} = 10, is shown in Fig. 6a. In the SEM photographs, the presence of two phases is clearly observed; a

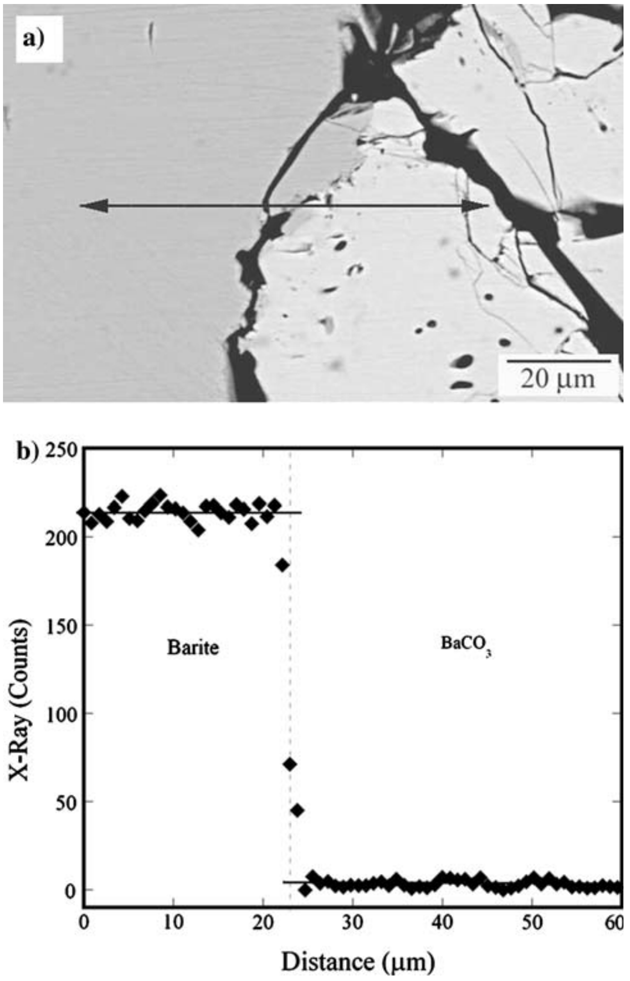

Fig. 6 (**a**) SEM image of the cross section of a partially converted barite crystal hydrothermally treated in a Na_2CO_3 solution with a molar ratio CO_3^{2-}/SO_4^{2-} = 10, at 250 °C for 24 h, and (**b**) Sulfur concentration profile determined over the distance between the arrows in Fig. 6a

phase with a significant amount of holes that is near the mineral surface, and a continuous phase inside the crystal. One point that must be emphasized is that the two phases are separated by a sharp boundary in texture, as well as composition. From this observation it is clear that the replacement reaction begins from the surface of the mineral that was in contact with the hydrothermal media. In addition, the reaction seems to proceed by the incorporation of the solvent through the inner porosity. The holes seem to form a zig-zag network inside the crystals which allows incorporating fresh solvent media at the reaction front [12, 13].

Hitherto, much research work has been focused on the ion exchange reaction of SO_4^{2-} by CO_3^{2-} in another related alkaline earth sulfate mineral, such as $SrSO_4$. During lixiviation processing the ion replacement process is achieved by a topochemical mechanism, which involves the formation of a solid $SrCO_3$ layer and a subsequent SO_4^{2-} diffusion through the dense $SrCO_3$ layer [4, 5]. However, the first real evidences that depict the ion exchange reaction of SO_4^{2-} by CO_3^{2-} proceeds at solid state conditions even under hydrothermal conditions were provided by Yoshino et al. [6]. They found that the CO_3^{2-}/SO_4^{2-} ion exchange, in celestite ($SrSO_4$) crystals which were in contact with witherite ($BaCO_3$) powder, is achieved at temperatures as low as 500 °C for 168 h at high pressure (100 MPa). Under these conditions, the anion motion proceeds through the crystalline structure of celestite crystals and witherite powders, and this is enhanced by an atomic diffusion mechanism. Indeed, the crystalline structural defects, namely vacancies or dislocations, play an important role on the ion exchange reaction at solid state conditions, because the motion of ions is accelerated due to the interaction between defects and ions [8, 9]. Therefore, the conversion investigated in the present work, does not proceed by a solid state ion exchange reaction, because it was conducted at lower temperature in comparison with that aforementioned in $SrSO_4$ crystals. In contrast, the present authors have recently reported that the conversion of $SrSO_4$ crystals into $SrCO_3$ was carried out at a low temperature (150 °C) in highly concentrated carbonated solutions under hydrothermal conditions. The conversion is achieved in this case by a pseudomorphic replacement process. This particular conversion process proceeds with the formation of a converted layer that has a peculiar texture (holes) and a moving reaction front. Based on our results, we surmise that the conversion of barite crystals into barium carbonate is promoted by a pseudomorphic replacement process rather than the ion-exchange process.

The high magnification SEM micrographs taken at the reaction interface on partially reacted barite crystals showed that the reacted layer consists of two different crystalline phases (Fig. 6a). In addition, a sulfur X-ray line profiles (Fig. 6b) were determined in the direction in which the conversion reaction advances inside the crystal, perpendicular to the crystal surface. The concentration profile revealed a marked difference on sulfur content between the new phase and the raw barite phase. The profile reveals that a single sharp boundary in sulfur composition was produced at the reaction interface. This boundary delimits the outer converted $BaCO_3$ layer and the inner mineral barite core. The results show that across the reaction boundary no sulfur diffusion gradient was revealed. Hence, the conversion studied in the present work cannot be associated with the ion exchange mechanism which is enhanced at solid state conditions. In contrast, in our particular case the pseudomorphic conversion $BaSO_4$ into $BaCO_3$ might be achieved by a dissolution-recrystallization mechanism, similar to the replacement process that lead to the conversion of other related earth alkaline sulfate minerals such as celestite [8, 14].

Conclusions

Mineral barite crystal plates (10 × 10 × 3 mm) were converted to barium carbonate under alkaline hydrothermal conditions. The reaction was accelerated by increasing the treatment temperature, autoclave filling ratio, and the solvent molar ratio. The mineral barite specie is chemically stable even at mild hydrothermal conditions (<200 °C), below this temperature the barite crystals partially reacted with the carbonated rich alkaline solvent. The conversion of $BaSO_4$ crystals into $BaCO_3$ crystals proceeds by the pseudomorphic replacement process, which is achieved by a dissolution-recrystallization mechanism. The complete conversion of the barite crystals proceeds at 250 °C for 192 h in a CO_3^{2-} rich solution (molar ratio $CO_3^{2-}/SO_4^{2-} = 10$). The total porosity formed during the conversion was found to be produced by a coupling bulk molar volume contraction of the crystalline structure and a partial dissolution of the $BaCO_3$ phase, due to the higher dissociation of this compound under alkaline conditions.

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