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# Rod shaped barium sulfate particles from a completely inorganic system

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## **Abstract**

Rod-shaped barium sulfate particles can be formed from purely inorganic systems at 75 °C and these particles are single crystals elongated in the *c*-axis. This *c*-axis growth promotion relative to the other crystal faces is absent when the cation impurities are absent suggesting a specific interaction of the cations with the growing crystal. Attempts have been made to determine the cause of this *c*-axis growth promotion, but no one mechanism appears to adequately explain this effect and it may be due to a combination of different impacts. The same cations do not induce rod shaped particles at 25 °C, thus suggesting an important role of kinetics in the crystallization of these particles. Finally, previous reports suggesting that the formation of rod like particles is due to the presence of an organic additive may be incorrect as sufficient sodium ions may have been present to give these particles even in their absence.

**Keywords:** A1 crystal morphology A2 growth from solutions A1 impurities B1 barium compounds B1 salts

## 1. Introduction

While much literature is focused on the effect impurities have on inhibition of crystallization, it is clear that promotion occurs and can be equally important.<sup>1-3</sup> It has long been a dream of technologists to be able to predict the impact an impurity will have on crystallization; to date, however, this remains elusive. Inhibition is most commonly investigated because this can be ascertained straightforwardly from experiments. However, even this area is open for further mechanistic understanding since there are those who report that ‘lattice matching’ is critical for inhibition<sup>4-6</sup> while others suggest that electrostatic but non-specific interactions are dominant<sup>7-9</sup>. Our own work has suggested a possible action of both with regards to inhibition.<sup>10</sup>

There has, however, been an apparent reticence to tackle the issue of kinetics within crystallization due to its inherent experimental difficulties but few would refute the importance of kinetics to overall crystallization processes. New work is, however, beginning to fill this gap<sup>1-3, 11, 12</sup>. This new focus on kinetics has renewed interest in the area of crystallization promotion of inorganic solids and, along with it, the desire to understand the promotion mechanisms. This work is in its infancy and there is still much to learn.

Barium sulfate has been a useful model system, owing to its lack of polymorphs and simple chemistry.<sup>13, 14</sup> In spite of this, the crystallization of barium sulfate is still able to throw up some interesting surprises. The molecular modeling of barium sulfate growth mechanisms on the (001), (210) and (010) faces<sup>15</sup> has shown that such fundamental atomistic knowledge on the crystallization mechanisms can be strategically used. For example, on a thermodynamic **surface energy** basis, the (010)

face is expected to be present in the morphology of barium sulfate but is hardly seen (except when impurities are present). This can be explained by the modeling since the (010) face is calculated to have the lowest activation energy barrier in the presence of sulfate and so is a kinetically fast growing face. Similarly, this work showed that the (001) face had a strongly adsorbed layer of molecular water present, thus impurities that could disrupt this barrier would promote (001) growth. This was indeed found experimentally when methanol was added.<sup>11, 12, 15</sup> Overall, the crystallization process was limited by the rate of barium ion dehydration, and thus, this information could be used to predict organic precipitation promoters for barium sulfate crystallization.<sup>16</sup>

Inorganic cations have also been investigated and some shown to promote crystallization of barium sulfate.<sup>17-21</sup> To date, as this literature demonstrates, cations shown to promote barium sulfate have been limited to +1 cations. Building on the hypothesis that crystallization promotion is a kinetic phenomenon, we can manipulate the kinetics of reactions by altering temperature<sup>22</sup> and in this manuscript we investigate what happens when we alter the significant driver of crystallization from thermodynamics (changes in enthalpy and entropy) to kinetics (changes in activation energy barriers). This paper, then, presents a preliminary, qualitative investigation into the morphological changes the presence of inorganic cation impurities have upon the crystallization behaviour of barium sulfate at different temperatures.

## 2. Experimental

The barium sulfate particles were precipitated in glass vials (25mL) and the total volume of all solutions was maintained at 20.0 mL. Solution containing the desired

cation at the desired concentration was placed in the vial. A washed, cleaned and dried (round) glass cover slip was added to the vial. Barium chloride (0.1 M or 0.01M) was added using a micropipette to achieve the desired concentration and then equilibrated to temperature (25 °C or 75 °C) in a water bath (from Thermoline Scientific). Finally, stoichiometric sodium sulfate (0.1 M or 0.01M) was added to commence the crystallization. After 3 days, the glass cover slips were removed, filter paper used to soak up excess solution, and prepared for microscopy. The supersaturation,  $S$ , value was calculated using the PHREEQC program<sup>23</sup> to account for ion pairing in solution and is defined as:

$S = (IAP/K_{sp})^{1/2}$  where the IAP is the ion activity product and  $K_{sp}$  is the solubility product. In some cases, the data from the PHREEQC calculation was used to determine the barium to sulfate ion ratio by taking the free barium ion concentration divided by the free sulfate ion concentration. **The addition of cations to the solution will lower the free sulfate ion concentration due to ion-pairing thus addition of cations to the system without adjustment of the barium or sulfate ion concentration will result in a lower  $S$  value.**

The results presented here are based on morphology alone, which may or may not be different to that expected based on more detailed considerations. However, morphology can certainly ascertain the *relative* importance of particular faces to the overall habit of the crystal. In this way, assuming that the slowest growing faces are the dominant faces, we can determine the relative rates of different crystal faces on barium sulfate. As shown in Figure 1 below, we can determine whether the  $c$ -axis of barium sulfate is either slow growing or fast growing compared to the other faces. In addition, table 1 lists all of the properties that may be useful in determining the

behaviour of cations on barium sulfate crystallization. Thus, in this morphological investigation the relative dominance of faces and not their absolute size is critical.

Figure 1 and Table 1 near here

### 2.1 Scanning Electron Microscopy (SEM) preparation

The glass cover slip was placed on a carbon coated SEM stub and carbon paint applied to the circumference to allow better conduction of charge to the stub (and thereby avoid excessive charging). The stub was then dried in a dessicator prior to gold sputtering and viewed on a Zeiss Evo or Phillips XL30 scanning electron microscope.

## 3. Results

The growth of barium sulfate is sensitive to the supersaturation and this results in morphological changes as  $S$  varies.<sup>27, 28</sup> The morphology was investigated both at 25 °C and 75 °C (the increase in temperature of the precipitation increases the effect of kinetics due to the Arrhenius relationship of the rate constant while the thermodynamics,  $\Delta G$ , change less significantly with temperature<sup>22</sup>). Table 2 shows the morphology of barite at varying  $S$  levels and when different amounts of cations are present (the calculated  $S$  value is given in brackets) at 75 °C.

Table 2 near here

Rod-shaped barite is not a common morphology unless the crystals are formed in the presence of emulsions<sup>29, 30</sup> (although those particles formed in emulsions are not

straight but curved, filamentous mesocrystals) or organic additives<sup>31, 32</sup>. It is clear that in the rod-shaped particles produced in this work, the *c*-axis is much longer than expected for the equivalent S value (the *c*-axis is specified on some particles by the double headed arrow) and therefore the (001) face is obviously a fast growing face relative to the other faces. This is supported by the sodium chloride result at S=5.82 where the morphology of the particles is the same as those at S=11.35 but the *c*-axis is much longer. In addition, +1 cations are known to promote barium sulfate crystallization at 25 °C.<sup>17, 19</sup>

There are also face specific and ion specific interactions. An example is when zinc ions are present (at 75 °C); this appears to lead to a longer *c*-axis length but also to larger (210) faces when compared to the equivalent control. There is also the appearance of the (211) chamfered face in many particles (Supplementary Information SIFigure 1). Thus, there is both an observed increase in the relative *c*-axis growth and a simultaneous decrease in the growth of the (210) and (211) faces. At 75 °C it is interesting to note that many cations can promote *c*-axis growth; some of the more pronounced are Al<sup>3+</sup>, Na<sup>+</sup> and K<sup>+</sup>. Even acid is shown to promote *c*-axis growth at high temperatures when compared to the similar S value (thermodynamic driving force).

Powder XRD (Figure 2a) on the rod-like particles formed in the presence of NaCl confirmed barium sulfate as the expected solid phase formed with no significant line broadening but with different peak height ratios when compared to a control (see supplementary information, SIFigure 2). This suggests that they are large single crystals and not agglomerates of smaller particles. The 020, 011, 211 and 401 peaks in

particular were greatly increased relative to the control. This suggests that the (010) and (h11) family of faces may be important. The existence of the chamfered faces when none are found in the control is consistent with the higher h11 peaks. The SEM image of the particles (Figure 2b) shows distinct (210) faces (highlighted on one particle) and it is possible that the absence of an enhanced 210 peak and the preference for the 020 peak is a preferred orientation effect known to occur for anisotropic particles.

Figure 2 near here

In the presence of lanthanum ions, barium sulfate particles show some significant rounding. In addition, there appeared to be a second population of particles that were slightly different in morphology (Figure 3). These particles are more defined and show distinct (210) faces. The two populations of particle shapes appeared equal in number.

Figure 3 near here

The situation at 25 °C is quite different to that at elevated temperature. At 25 °C the aspect ratio of the barium sulfate particles varies more significantly with supersaturation (Table 3). At low supersaturations the aspect ratio is quite small, ~1:2 while at high supersaturations it is quite high ~1.5:1 (length to width). Thus, as



supersaturation increases the length of the *c*-axis also increases (the *c*-axis is highlighted by the yellow arrows).

The addition of NaCl induced the particles to become more square-like. Other ions also showed a more 1:1 aspect ratio. The particles formed at high NaCl levels also have distinct (210) faces (albeit small ones). In particular, the particles formed at high NaCl levels show many growths out of the (hk0) planes suggesting there is twin formation. Calcium ions are known to incorporate into the barium sulfate lattice and form very flat but rhombic shaped particles.<sup>33, 34</sup> Thus, ions that incorporate do not appear to show *c*-axis lengthening but this may depend on the specific effect of the ion on the individual lattice parameters.

Table 3 near here

For many of the cations, there is no *c*-axis lengthening at 25 °C, in fact it appears shorter at lower S values (higher cation concentration). Yet ions that we would suspect should promote *c*-axis growth at this temperature (such as Cs<sup>+</sup>) show twinning as per the sodium ion. The effect on the *c*-axis is much diminished overall. Those ions that are known or suspected to incorporate (Ca<sup>2+</sup>, La<sup>3+</sup>) show pronounced inhibition of the *c*-axis at room temperature as seen for calcium at elevated temperature. This incorporation was confirmed by XRD lattice parameter determination.<sup>35</sup> In the case of La<sup>3+</sup> ions being present, inhibition of barium sulfate crystallization was expected at 75 °C (based on 25 °C results), but determination of the impact on the *c*-axis was difficult. If we assume a length for the control similar to that shown for S~6 in the absence of additional cations then there is little difference between these and the

particles' *c*-axis as shown in Fig 2a. This could be because the thermodynamic driving force for incorporation is weaker at elevated temperatures *or* there are face specific interactions occurring and the greatest impact is not on the *c*-axis (this is supported by the morphology change observed of the particles).

The 25 °C results are much more sensitive to concentration effects. Generally speaking, at 25 °C, when the concentration of the cation is high enough to reduce the *S* value to below ~17 from the original value of ~19, *c*-axis shortening is observed (see Figure 4 for the case of magnesium ions).

Figure 4 near here

#### 4. Discussion

From the tables shown above we can clearly see that rod-shaped particles from purely inorganic systems can be easily achieved at elevated temperatures. This suggests an alternative explanation for some previous work where the organic additive was seen as causing this particular morphology to form.<sup>31, 32</sup> The concentration of sodium ions from the EDTA alone in these earlier reports is approximately 0.05M while in this work we used ~0.08 M at the highest concentration. Given that crystallisation was also carried out at elevated temperatures (90-150 °C<sup>31, 32</sup> versus 75 °C in this work) it is possible that the rod shaped particles reported are due to the sodium ions alone.

As supersaturation increases the *c*-axis length is also seen to increase. This occurs at both 25 and 75 °C and is due to the greater proportion of ions that can penetrate the strongly adsorbed water layer on the (001) as *S* increases.(our ref) In addition, since

this is a kinetic barrier, associated with the ability of the ions to move through this physical barrier and not to changes in entropy or enthalpy, we see this  $c$ -axis lengthening at lower  $S$  values when the temperature is higher. Given that we do not see rod shaped particles in the absence of cations, we can assume that the presence of cations must, therefore, be critical.

There appears to be a large number of cationic species that can promote  $c$ -axis growth resulting in rod-shaped particles, thus, cation charge appears to be a secondary parameter. In addition, face specific interactions are also observed, such as the large flat (100) face observed in the presence of  $\text{Cs}^+$ . Thus, adsorption of ions onto certain faces (such as the (210)) may slow faces down causing a relative increase in the (001) face growth rate. Finally, the fact that rod shaped particles are only observed at 75 °C suggests that their formation is somehow connected to changes in the kinetics of crystallization.

There has been literature in the past relating the extent of promotion to the chloride salt solubility.<sup>20</sup> However, this does not work for predicting inhibition. For example, calcium ions have been shown to inhibit crystallization at 25 °C<sup>33, 34</sup> but its chloride salt is quite soluble (81.3 g/100g water, see Table 1) while lithium ions promote crystallization<sup>20</sup> and yet the chloride salt solubility is quite similar (see Table 1, 84.5g/100g water). It is tempting to say that a better indicator is the sulfate salt solubility, with those cations with low sulfate salt solubilities being the ones that will inhibit more effectively. In this case, however, potassium ions would be expected to inhibit, which is clearly not the case. Thus, neither the chloride salt nor the sulfate salt

solubility is able to adequately predict inhibition *and* promotion by any particular cation.

Another possible predictor of crystallization promotion is the impact these ions will have on the barium ion:sulfate ion ratio.<sup>19</sup> Higher ratios have been found to increase the growth rate of the (001) (which is the *c*-axis) and therefore could explain the observations here. The barium ion to sulfate ion ratio has been calculated for **some experiments** and listed below the SEM images in Table 2 in italics. Clearly, this too, is not sufficient to explain the *c*-axis lengthening observed. For example, we would assume that the greatest *c*-axis lengthening would occur for the highest barium ion to sulfate ion ratios. If we look at only those particles formed at an S value of ~9.4 and 75 °C (in the presence of zinc, magnesium and calcium ions) we see that the presence of zinc ions still has a greater effect than magnesium ions despite the barium ion:sulfate ions ratio being higher for the magnesium ion system. In addition, regardless of the barium to sulfate ion ratio, if a cation incorporates (such as calcium), then this dominates the effect on morphology. Thus, the barium ion/sulfate ion ratio is not sufficient to predict *c*-axis lengthening. The observation of a fast growing *c*-axis then must be related to some other cause.

**While it is clear that a kinetic energy barrier is being altered by the presence of these cations**, the barrier being 'catalysed' by the presence of these cations is something other than the de-solvation of the barium ions unless the presence of the cations alters the water structure so significantly as to aid de-hydration of barium. The impact of ions on water structure is often described in terms of the ions being kosmotropes or chaotropes<sup>19, 21</sup> however, the promotion of *c*-axis growth by the presence of +1, +2

and +3 ions suggests that this too is not the determining factor. It may be a combination of effects such as the impact these ions have on water structure, the barium ion:sulfate ion ratio, and possible stabilization of kinks and face specific interactions. However, experimental evidence for this will be difficult to obtain and molecular dynamics will be the best mode of investigating these possible mechanisms.

The concentration effect at 25 °C is not unexpected and can be understood in terms of a simple equilibrium argument. At higher concentrations, the equilibrium will favour adsorption processes especially for those with  $K_{ads} > 1$ . Adsorption at growth features such as kinks and steps will result in inhibition of growth. Given that the log K for complexation in solution can be an indicator of interactions species have with surface groups<sup>36</sup> it should also give the likelihood and strength of adsorption of these species onto the surface. It is naturally dependant on the charge density or hydrophobicity of the impurity as discussed in the literature.<sup>1-3</sup> For the +1 cations, their log K values are generally less than 1 and so promotion is observed for these cations even at quite high concentrations. At higher concentrations then, *c*-axis shortening due to adsorption at growth features would be expected and this is observed. At this temperature, then, the log K value becomes more important as thermodynamic effects, such as adsorption, dominate.

One important factor that has not been taken into consideration in this work, however, has been the enthalpy of adsorption of the cation to the surface, which will also have a significant impact particularly when temperature is altered. If adsorption of the cation to the barium sulfate surface is exothermic then temperature increases will favour

desorption and vice versa. Clearly, the favouring or otherwise of the adsorption process will be an important variable. There are adsorption phenomena occurring even at elevated temperatures as is clear by the stabilization of faces such as the (211) and (210) faces. In addition, crystallization promotion can be difficult to ascertain from morphology changes alone. A case in point is  $\text{La}^{3+}$  which is known to incorporate and inhibit barium sulfate crystallization at 25 °C but shows no *c*-axis lengthening or shortening in comparison to the ‘control’ at 75 °C. Thus, does  $\text{La}^{3+}$  inhibit or promote growth of barium sulfate at 75 °C? Also, the aluminium ions do not show a significant shortening of the *c*-axis at room temperature even when the aluminium ion concentration present is high. Thus, the room temperature behaviour can also be difficult to interpret. However, the fact that these experiments were carried out at pH 6 meant that  $\text{Al}(\text{OH})_3$  could co-precipitate and PHREEQC<sup>18</sup> did calculate that the solution would be supersaturated with regard to this species. Thus, these results may not be due to barium sulfate crystallization alone and seeding or templating effects may also be present.

While water structure no doubt plays a part in the kinetics of crystallization and the promotion of it, it does not predict cation promotion *and* inhibition (particularly for the cations with charges greater than one). Similarly, the lengthening of the *c*-axis, while of interest, does not determine overall promotion of crystallization but merely relates to *c*-axis growth relative to other crystal faces. Thus, in addition to this work, quantitative experimental data (such as growth rates) at 75 °C should also be obtained. However, this is not a trivial exercise.

## 5. Conclusions

The morphology of barium sulfate can be used to determine the impact on the *c*-axis growth rate *relative* to other faces. This work has shown that many cations have the ability to promote *c*-axis growth at elevated temperatures and that this cannot be explained by chloride salt solubility, sulfate salt solubility or kosmotrope/chaotrope behaviour on water structure alone. Thus, at the elevated temperature no one mechanism appears to adequately explain the impact on morphology based solely on a morphological examination.

Given the lack of similar impacts of these cations on the crystallization of barium sulfate at room temperature, we can conclude that the impact at 75 °C is predominantly due to kinetic effects (changes in activation energy barriers). We note that in the absence of cations, no rod shaped particles are formed, illustrating that both the cations and the elevated temperature are a necessary requirement for the rod shaped particles to exist.

Barium sulfate has been shown to grow in long rod-like particles quite different to the mesocrystal fibres previously described in literature. These appear to be single crystal in nature and not nanoparticulate. In addition they are formed in the absence of organic additives. Thus, this relatively simple inorganic regime can deliver particles that were previously thought to be due to the presence of organic impurities.<sup>31, 32</sup> In fact, it is unclear whether the formation of rods in previous literature is actually due to the presence of EDTA (ethylenediaminetetraacetic acid) or whether it was due to the presence of a sufficient concentration of sodium ions.

Finally, this qualitative study is based on morphology alone so it would be of interest to obtain more direct information on the growth of the (001) face of barium sulfate in the presence of these cations at elevated temperature by AFM measurements in order to validate these findings.

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