



# Ionothermal synthesis of the mixed-anion material, $\text{Ba}_3\text{Cl}_4\text{CO}_3$

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## ABSTRACT

A low-temperature ionothermal method for the facile synthesis of the halide carbonate,  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ , in single-crystalline form has been developed. This has enabled the first determination of the crystal structure of this material to be carried out. Analysis of single-crystal X-ray diffraction data indicates that barium chloride carbonate crystallises in the orthorhombic space group  $Pnma$  ( $Z = 4$ ), with  $a = 8.4074(11)$ ,  $b = 9.5886(12)$ ,  $c = 12.4833(15)\text{Å}$  ( $R_w = 0.0392$ ). It exhibits a complex structure in which a three-dimensional network is formed from cross-linking of chains of anion-centred octahedra that share faces.

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## 1. Introduction

Low-temperature synthetic methods are increasingly being explored as alternatives to conventional high-temperature processes for the preparation of inorganic materials. Reactions carried out at relatively modest temperatures frequently afford access to novel materials that may be kinetically stabilised and therefore not accessible at elevated temperatures. Amongst the range of approaches that has been adopted are intercalation, sol-gel methods, ion exchange, reactive fluxes and solvothermal synthesis [1]. Solvothermal methods in particular have proven to be an extremely versatile technique for the synthesis of a diverse range of novel materials including, silicates, phosphates, oxides, selenides and sulphides [2].

More recently, researchers have begun to exploit ionic liquids as reaction media for the synthesis of inorganic materials. Ionic liquids [3,4] may be defined as salts that melt below  $100^\circ\text{C}$ . Their solvent properties are determined by the ability of the salt to act as a hydrogen-bond donor and/or acceptor and by the degree of localisation of the charge on the anion. Their unique properties, which include high polarity, conducting nature, low vapour pressure and viscosity, have already led to their adoption as 'green' solvents for conventional organic synthesis [5,6]. They have also been exploited in electrochemistry, batteries, fuel cells, photovoltaic devices and electrodeposition processes [3,7–9]. Extension to inorganic systems [10], including the preparation of nanoparticulate fluorides [11] and sulphides [12] has been reported. Furthermore, the tailored synthesis under ionothermal

conditions of materials containing nanopores and channels [13], including hierarchical ZnO nanostructures [14], mesoporous  $\text{SrCO}_3$  spheres,  $\text{CaCO}_3$  hollow spheres [15] and mesoporous silica and Ru-SiO<sub>2</sub>, [16] has recently been described. The first report [17] of the synthesis of an aluminophosphate in the presence of an ionic liquid has stimulated efforts to create new microporous materials in such reaction media. By contrast with conventional solvothermal reactions, the ionic liquid in ionothermal synthesis acts as both solvent and template, and therefore greater control of the templating process may be achieved. In addition to a number of aluminophosphates and zeolites [18], ionothermal methodologies have recently been used to facilitate the synthesis of coordination polymers [19] and metal-organic frameworks [20].

In an extension of our established programme of solvothermal synthesis of inorganic materials, we have recently begun to explore the use of ionic liquids as reaction media for low-temperature synthesis. During the course of efforts to extend the oxy-anion chemistry in ionic liquids to transition-metal carbonates, we have prepared  $\text{Ba}_3\text{Cl}_4\text{CO}_3$  in 1-ethyl-3-methylimidazolium bromide (EMIB) at  $170^\circ\text{C}$ . This appears to be the first ionothermal synthesis of a mixed-anion material. Although  $\text{BaCl}_4\text{CO}_3$  was first reported by Frit et al. [21] as arising from the high-temperature ( $850^\circ\text{C}$ ) reaction of  $\text{BaCl}_2$  and  $\text{BaCO}_3$  in a  $\text{CO}_2$  atmosphere, the polycrystalline nature of the product has prevented determination of the crystal structure for over 40 years. Remarkably, low-temperature synthesis in EMIB at  $170^\circ\text{C}$  yields good-quality single crystals, allowing the first structure determination of this category of mixed-anion material to be accomplished. The results demonstrate that  $\text{BaCl}_4\text{CO}_3$  adopts a structure of surprising complexity, which may be described in terms of chains of anion-centred polyhedra.

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## 2. Experimental

Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> was synthesised from a mixture of the ionic liquid 1-ethyl-3-methylimidazolium bromide (Aldrich, 0.5 g, 2.62 mmol), BaCO<sub>3</sub> (Johnson Matthey, 99.9%, 0.065 g, 0.33 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 98%, 0.084 g, 0.66 mmol) with a molar composition BaCO<sub>3</sub>:CoCl<sub>2</sub>·6H<sub>2</sub>O:EMIB of 1:2:8. The mixture was placed in a Pyrex tube and the contents frozen with liquid nitrogen. The tube was evacuated to 1 Torr prior to sealing. The sealed tube was placed in an oven, heated at 170 °C for 3 days and then cooled to room temperature at a rate of 1 °C min<sup>-1</sup>. The product was filtered, washed with methanol and acetone and dried in an oven at 90 °C in air at room temperature. The solid product appears to consist of a mixture of colourless needles, identified by single-crystal X-ray diffraction as Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub>, and an inhomogeneous powder, identified by powder X-ray diffraction (Bruker D8 Discover, CuKα radiation, λ = 1.5418 Å) as a mixture of starting materials, BaCO<sub>3</sub> and CoCl<sub>2</sub>·2H<sub>2</sub>O. Efforts to produce a phase-pure sample by exploring a wide range of reaction parameter space were unsuccessful. Longer reaction times led to a solid product which consisted only of BaCO<sub>3</sub>. Subsequently, in an effort to produce a single-phase product, a series of reactions, in which the CoCl<sub>2</sub>·6H<sub>2</sub>O was omitted, was performed for a range of BaCO<sub>3</sub>:BaCl<sub>2</sub>:EMIB molar ratios. In all cases only BaCO<sub>3</sub> powder was present in the solid product, indicating that the transition-metal chloride is essential for the formation of the title compound. A similar feature has been observed previously in the synthesis, under solvothermal conditions, of [C<sub>6</sub>H<sub>20</sub>N<sub>4</sub>][Sb<sub>4</sub>S<sub>7</sub>], for which the presence of either cobalt [22] or zinc [23] ions is required to produce the product phase. As it was not possible to remove the BaCO<sub>3</sub> contaminant, conventional analytical techniques such as thermogravimetry and combustion analysis provide no additional useful information.

A crystal of Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> (dimensions 0.18 × 0.18 × 0.20 mm) was mounted on a glass fibre using cyanoacrylate adhesive. X-ray intensity data were collected at 293 K using a Bruker X8-APEX CCD diffractometer [24] with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were processed using the manufacturer's standard routines [25]. Full crystallographic details are given in Table 1. The structure was solved using the direct methods program SIR92 [26], which located barium and chloride ions. Subsequent Fourier calculations and least-squares refinements against *F* were carried out with the CRYSTALS suite

of programs [27]. The carbon and oxygen atoms were located in difference Fourier maps. In the final cycles of refinement, anisotropic thermal parameters were refined for all atoms. A three-term Chebyshev polynomial was applied as a weighting scheme [28].

## 3. Results and discussion

The local coordination and atom labelling scheme for Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> is shown in Fig. 1, whilst fractional atomic coordinates are given in Table 2. Selected bond distances and valence sums [29] are presented in Table 3. Each of the two crystallographically-distinct barium ions is effectively nine-coordinate. Ba(1) has six chloride neighbours at ca. 3.15 Å, with a seventh at the longer distance of 3.467(2) Å. Two carbonate ions, one acting as a monodentate ligand, the other as a bidentate ligand, at Ba–O distances of ca. 2.75 Å, complete the first coordination sphere of Ba(1). The second barium ion, Ba(2), also has six neighbouring chloride ions, at distances in the range 3.265(2)–3.371(2) Å, together with three oxygen atoms associated with two carbonate ions, one monodentate, the other bidentate, at Ba–O distances in the range 2.751(6)–2.800(6) Å. The Ba–Cl distances are generally comparable with those reported for BaCl<sub>2</sub> [30] and consistent with the sum of the ionic radii (3.16 Å) [31]. The additional chloride ion, Cl(1), at a longer distance of 3.467(2) Å; contributes only 0.12 valence units to the valence sum. Ba–O distances are consistent with those in BaCO<sub>3</sub> [32], but somewhat

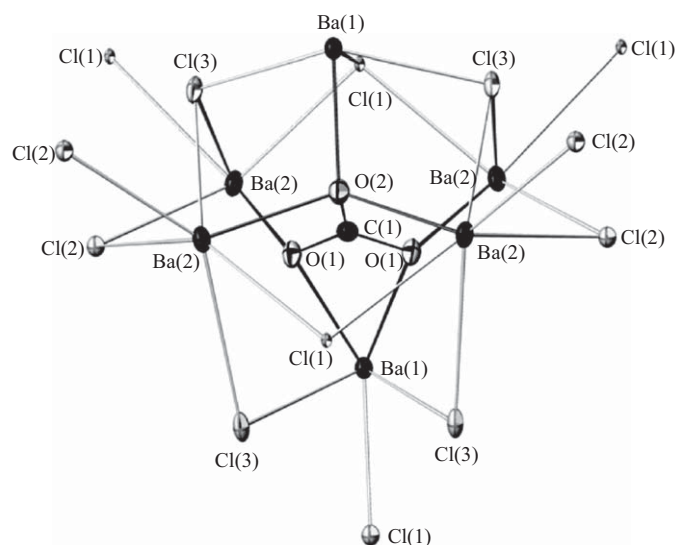


Fig. 1. Local coordination of Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> showing the atom labelling scheme and thermal ellipsoids at 50% probability.

Table 1  
Crystallographic data for Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub>.

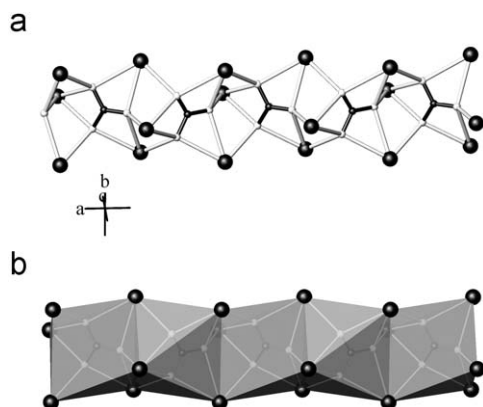
Formula	Ba <sub>3</sub> Cl <sub>4</sub> CO <sub>3</sub>
<i>M<sub>r</sub></i>	613.84
Dimensions (mm)	0.18 × 0.18 × 0.20
Crystal habit	Colourless block
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>T</i> (K)	293
<i>a</i> (Å)	8.4074(11)
<i>b</i> (Å)	9.5886(12)
<i>c</i> (Å)	12.4833(15)
<i>V</i> (Å <sup>3</sup> )	1006.3(2)
<i>Z</i>	4
μ (mm <sup>-1</sup> )	12.628
ρ <sub>cal</sub> (g cm <sup>-3</sup> )	4.05
Measured data	25 333
Unique data	1540
Observed data ( <i>I</i> > 3σ( <i>I</i> ))	933
Residual electron density (min, max) (eÅ <sup>-3</sup> )	–1.71, 4.70
<i>R</i> <sub>merg</sub>	0.0405
<i>R</i>	0.0346
<i>R</i> <sub>w</sub>	0.0392

Table 2  
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub>.

Atom		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
Ba(1)	4(c)	0.95666(8)	$\frac{3}{4}$	0.96465(5)	0.0165
Ba(2)	8(d)	0.05228(5)	0.99295(4)	0.31929(4)	0.0188
Cl(1)	4(c)	0.0455(3)	$\frac{3}{4}$	0.51399(15)	0.0084
Cl(2)	4(c)	–0.1601(3)	$\frac{3}{4}$	0.20467(19)	0.0152
Cl(3)	8(d)	0.1973(2)	0.54076(18)	0.07696(15)	0.0201
C(1)	4(c)	0.7224(13)	$\frac{3}{4}$	0.7134(8)	0.0154
O(1)	8(d)	0.6557(7)	0.6331(5)	0.6876(4)	0.0195
O(2)	4(c)	0.8584(11)	$\frac{3}{4}$	0.7588(7)	0.0216

**Table 3**Selected bond distances (Å) and bond valences (v.u.) for Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub>.

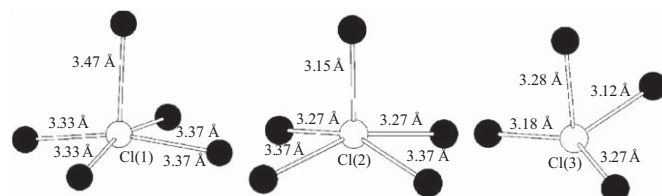
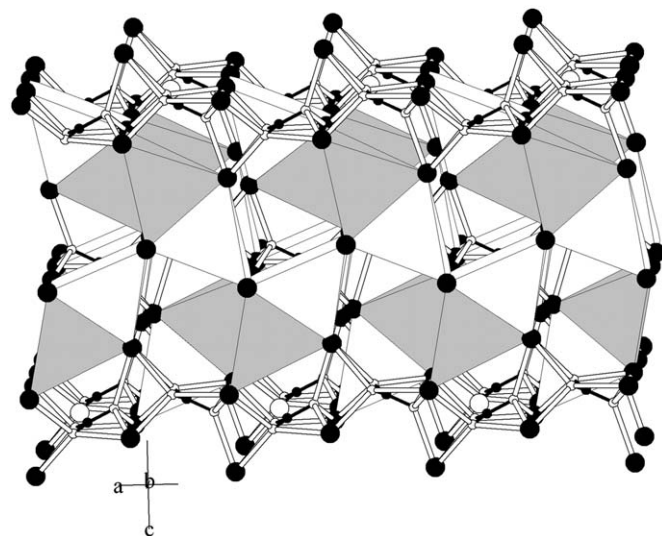
Atoms	Bond distances	v <sup>a</sup>
Ba(1)–Cl(1)	3.467(2)	0.122
Ba(1)–Cl(2)	3.153(3)	0.286
Ba(1)–Cl(3)	2 × 3.176(2)	2 × 0.269
Ba(1)–O(1)	2 × 3.118(2)	2 × 0.315
Ba(1)–O(2)	2 × 2.770(5)	2 × 0.274
Valence sum		2.456
Ba(2)–Cl(1)	3.367(1)	0.160
Ba(2)–Cl(2)	3.329(1)	0.178
Ba(2)–Cl(3)	3.265(2)	0.211
Ba(2)–O(1)	3.371(2)	0.159
Ba(2)–O(2)	3.269(2)	0.209
Ba(2)–O(1)	3.278(2)	0.204
Ba(2)–O(2)	2.800(6)	0.252
Ba(2)–O(2)	2.751(6)	0.288
Ba(2)–O(2)	2.755(4)	0.284
Valence sum		1.945
C(1)–O(1)	2 × 1.294(7)	
C(1)–O(2)	1.276(14)	

<sup>a</sup> Bond valence and their sums calculated using parameters from Ref. [29].**Fig. 2.** A single chain of carbonate centred CBA<sub>6</sub> octahedra. (a) Ball and stick representation and (b) polyhedral representation. (O, small open circles; C, small solid circles; Ba, large solid circles).

longer than the average Ba–O distance (2.52 Å) in the oxy-chloride Ba<sub>4</sub>OCl<sub>6</sub> [33].

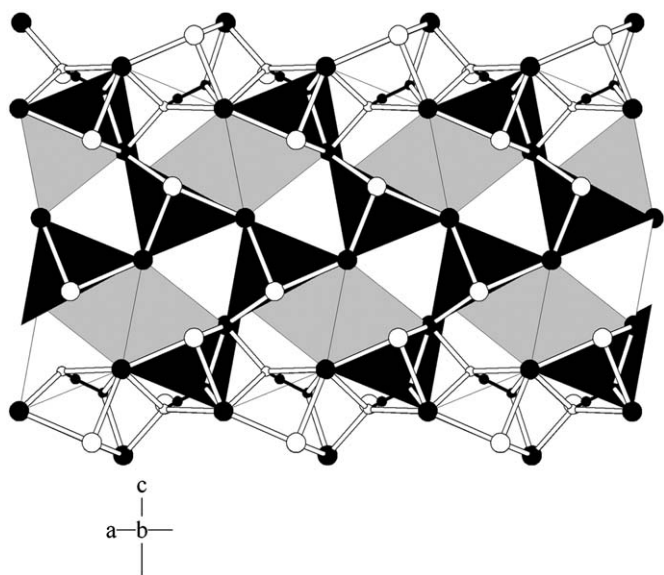
The barium and carbonate ions define a chain directed along [100], in which each oxygen atom of the carbonate ion exhibits  $\mu_3$  coordination to two Ba(1) and one Ba(2) ions (Fig. 2a). The carbon atom of each of the carbonate ions resides at the centre of a distorted octahedron of barium ions and the chains can thus be considered to consist of carbon-centred CBA<sub>6</sub> octahedra that share common faces (Fig. 2b). The CBA<sub>3</sub> chains of face-sharing CBA<sub>6</sub> octahedra are cross-linked by chloride ions, the local coordination polyhedra of which, together with bond distances to the barium ions are shown in Fig. 3.

Neighbouring CBA<sub>6</sub> chains in the [011] and [0 $\bar{1}$ 1] directions are linked by Cl(1) ions. Each Cl(1) is coordinated to five Ba<sup>2+</sup> ions in a square pyramidal geometry. Ba(2) in a given chain is at the apex of the Cl(1)Ba<sub>5</sub> pyramid, whose base is formed from Ba(1) ions, two from the same CBA<sub>3</sub> chain, and one from each neighbouring chain in two perpendicular directions. The Cl(1)Ba<sub>5</sub> square pyramids share basal edges to form chains directed along [010] in which the direction of the apex alternates along the chain direction (Fig. 4).

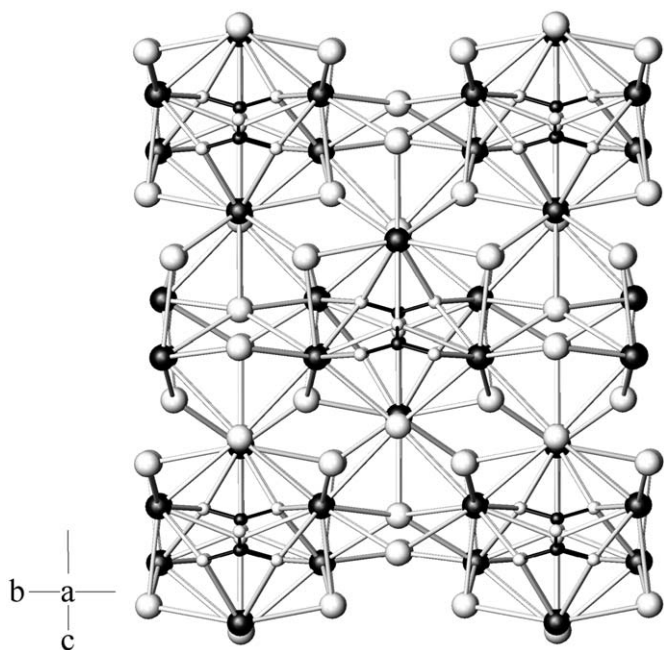
**Fig. 3.** Local coordination and atom–atom distances of the three crystallographically distinct ClBa<sub>n</sub> polyhedra that serve to link individual CBA<sub>3</sub> chains.**Fig. 4.** Cross-linking of barium carbonate chains by linear chains of Cl(1)-centred square-based pyramids directed along [010] and zigzag chains of Cl(2)-centred square-based pyramids. (Cl, large open circles; Ba, large solid circles; O, small open circles; C, small solid circles; Cl(1) square-base pyramids, grey and Cl(2) square-based pyramids, white).

Cl(2) also has a square-pyramidal coordination, having a Ba(2) apex that is shared with the Cl(1)-centred polyhedral chain and a base again formed from Ba(1) ions in neighbouring CBA<sub>3</sub> chains (Fig. 4). Cl(2)Ba<sub>5</sub> square-based pyramids form a zigzag chain directed along [100], which shares both edges and faces with the Cl(1)-containing chains that are aligned in a perpendicular direction. Four-coordinate (2 × Ba(1) and 2 × Ba(2)) Cl(3) ions, complete the cross-linking (Fig. 5): each tetrahedron containing three barium ions from one CBA<sub>3</sub> chain, with the fourth, located in a neighbouring chain, providing a common vertex that serves to link tetrahedra into a chain along [010]. The complex three-dimensional structure of Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> that results is represented in Fig. 6.

The chloride carbonate whose low-temperature synthesis and structure determination is reported here represents an example of a comparatively rare class of mixed-anion compounds. Amongst the small number of halide carbonates whose structures have been determined are phosgenite, Pb<sub>2</sub>Cl<sub>2</sub>CO<sub>3</sub> [34] and its bromide analogue [35]. However, in contrast to the complex three-dimensional structure of Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> reported here, phosgenite adopts a pseudo-layered structure in which two-dimensional Pb<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> slabs are connected by CO<sub>3</sub><sup>2-</sup> ions. The fluorinated analogue of phosgenite, Pb<sub>2</sub>F<sub>2</sub>CO<sub>3</sub> [36], exhibits a different architecture from that of the layered chloro- and bromo derivatives and is isostructural with the mineral Brenkite, Ca<sub>2</sub>F<sub>2</sub>CO<sub>3</sub> [37]. In common with Ba<sub>3</sub>Cl<sub>4</sub>CO<sub>3</sub> reported here, this



**Fig. 5.** Chains of edge-sharing  $\text{ClBa}_5$  square pyramids and  $\text{ClBa}_4$  tetrahedra, showing the cross-linking in the structure of  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ . (Cl(1) square-based pyramids, grey; Cl(2) square-based pyramids, white; Cl(3) tetrahedra, black).



**Fig. 6.** Three-dimensional network of  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ . (Cl, large open circles; Ba, large solid circles; O, small open circles; C, small solid circles).

lead fluoride carbonate also adopts a complex structure, although in this case the fundamental building units are infinite spiral chains of edge-sharing  $\text{FPb}_4$  tetrahedra, linked through common vertices to form a cationic three-dimensional network, in the tunnels of which are located the carbonate ions. This contrasts with  $\text{Ba}_3\text{Cl}_4\text{CO}_3$  in which the carbonate ions are an integral part of the polyhedral chain-like building units. Anion-centred polyhedra are also found in  $\text{Tl}_3\text{FCO}_3$  [38], which may be considered to comprise chains of face-sharing fluoride-centred octahedra, with cations residing in seven-coordinate sites of capped octahedral geometry. In contrast with  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ , rare-earth fluoro-carbonates, which represent perhaps the structurally best-

characterised members of this family of materials, tend to exhibit layered structures [39]. For example, the structure of  $\text{CeFCO}_3$  consists of alternating  $[\text{CeF}]$  and  $[\text{CO}_3]$  layers, whilst the structurally related  $\text{CaCe}_2(\text{CO}_3)_3\text{F}_2$  and  $\text{CaCe}(\text{CO}_3)_2\text{F}$  contain  $[\text{Ce}(\text{CO}_3)_2\text{F}]$  layers separated by  $\text{Ca}^{2+}$  cations [39,40].

Many of the known halide carbonates have been prepared under supercritical hydrothermal conditions [35,39] or by high-temperature reactions in a  $\text{CO}_2$  atmosphere [21]. In the present work, the first determination of the crystal structure of  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ , and hence on the basis of powder diffraction data, those of the analogous bromides and chlorides [41] has been made possible through the provision of good-quality single crystals via the low-temperature synthetic technique of ionothermal synthesis. Reaction under ionothermal conditions offers considerable scope for the production of inorganic materials. However, the role played by the ionic liquid in such reactions is poorly understood at present. In particular, it is unclear whether the ionic liquid acts solely as a solvent or plays a structure-directing role. In the reaction described here, clearly the EMIB is not incorporated into the final product so does not act as a conventional templating agent; however, a more subtle structure-directing role cannot be ruled out. It is perhaps notable that during the course of efforts to optimise the synthetic procedure the use of high-quality anhydrous reagents did not permit the synthesis of  $\text{Ba}_3\text{Cl}_4\text{CO}_3$ , suggesting that trace amounts of water, either present in the ionic liquid or as water of crystallisation in the transition-metal salt are required for the reaction to proceed. Water has been found to play a crucial role in the ionothermal synthesis of microporous materials when present in reagent quantities [42] and it has been suggested that it may act as a mineraliser [18]. At low levels, water may promote hydrolysis reactions [42], facilitating the production of solution-active species, thereby accelerating the kinetics of crystallisation.

### Supporting information

X-ray crystallographic information file (CIF), selected angles for  $\text{Ba}_3\text{Cl}_4\text{CO}_3$  and powder X-ray diffraction data can be found in the on-line version.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [10.1016/j.jssc.2009.06.019](https://doi.org/10.1016/j.jssc.2009.06.019).

### References

- [1] J. Gopalakrishnan, *Chem. Mater.* 7 (1995) 1265–1275.
- [2] P.A. Wright, *Microporous Framework Solids*, The Royal Society of Chemistry, Cambridge, UK, 2008.
- [3] T. Welton, *Chem. Rev.* 99 (1999) 2071–2083.
- [4] J.S. Wilkes, *Green Chem.* 4 (2002) 73–80.
- [5] T. Welton, *Coord. Chem. Rev.* 248 (2004) 2459–2477.
- [6] M.A.P. Martins, C.P. Frizzo, D.N. Moreira, N. Zanatta, H.G. Bonaccorso, *Chem. Rev.* 108 (2008) 2015–2050.
- [7] C.M. Gordon, *Appl. Catal. A* 222 (2001) 101–117.
- [8] J.D. Holbrey, K.R. Seddon, *Clean Products Process.* 1 (1999) 223–237.
- [9] R.D. Rogers, K.R. Seddon (Eds.), *Ionic Liquids: Industrial Applications for Green Chemistry*, ACS Symposium Series, vol. 818, American Chemical Society, Washington, DC, 2002.

- [10] A. Taubert, Z. Li, Dalton Trans. (2007) 723–727.
- [11] D.S. Jacob, L. Bitton, J. Grinblat, I. Felner, Y. Kolytyn, A. Gedanken, Chem. Mater. 18 (2006) 3162–3168.
- [12] Y. Jiang, Y.-J. Zhu, J. Phys. Chem. B 109 (2005) 4361–4364.
- [13] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, Angew. Chem. Int. Ed. 43 (2004) 4988–4992.
- [14] H.G. Zhu, J.F. Huang, Z.W. Pan, S. Dai, Chem. Mater. 18 (2006) 4473–4477.
- [15] J. Du, Z. Liu, Z. Li, B. Han, Y. Huang, J. Zhang, Microporous Mesoporous Mater. 83 (2005) 145–149.
- [16] K. Zhu, F. Pozgan, L. D'Souza, R.M. Richards, Microporous Mesoporous Mater. 91 (2006) 40–46.
- [17] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R.E. Morris, Nature 430 (2004) 1012–1016.
- [18] E.R. Parnham, R.E. Morris, Acc. Chem. Res. 40 (2007) 1005–1013.
- [19] K. Jin, X. Huang, L. Pang, J. Li, A. Appel, S. Wherland, Chem. Commun. (2002) 2872–2973.
- [20] D.N. Dybtsev, H. Chun, K. Kim, Chem. Commun. (2004) 1594–1595.
- [21] B. Frit, B. Tanguy, P. Hagenmuller, Bull. Soc. Chim. Fr. 1 (1967) 234–237.
- [22] P. Vaquero, D.P. Darlow, A.V. Powell, A.M. Chippindale, Solid State Ionics 172 (2004) 601–605.
- [23] A. Puls, M. Schaefer, C. Näther, W. Bensch, A.V. Powell, S. Boissière, A.M. Chippindale, J. Solid State Chem. 178 (2005) 1171–1181.
- [24] Bruker X8 APEX 2, Version 1.0-8, Bruker AXS Inc., Madison, WI, USA, 2003.
- [25] APEX-2 software, Version 1.27, Bruker AXS Inc., Madison, WI, USA, 2005.
- [26] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. Sect. A 27 (1994) 435–436.
- [27] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, CRYSTALS Issue 10, Chemical Crystallography Laboratory, University of Oxford, UK, 1996.
- [28] J.R. Carruthers, D.J. Watkin, Acta Crystallogr. Sect. A 35 (1979) 698–699.
- [29] N.E. Brese, M. O'Keeffe, Acta Crystallogr. Sect. B 47 (1991) 192–197.
- [30] E.B. Brackett, T.E. Brackett, R.L. Sass, J. Phys. Chem. 67 (1963) 2132–2135.
- [31] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751–767.
- [32] J.P.R. Villiers, Am. Mineral. 56 (1971) 758–766.
- [33] B. Frit, B. Holmberg, J. Galy, Acta Crystallogr. Sect. B 26 (1970) 16–19.
- [34] G. Giuseppetti, C. Tadini, Tscherms Mineral. Petrogr. Mitt. 21 (1974) 101–109.
- [35] A.G. Al'-Ama, E.L. Belokoneva, O.V. Dimitrova, V.S. Kurazhkovskaya, N.N. Mochenova, Russ. J. Inorg. Chem. 51 (2006) 1176–1180.
- [36] B. Aurivillius, Acta Chem. Scand. A 37 (1983) 159–160.
- [37] U. Leufer, E. Tillmanns, Tscherms Mineral. Petrogr. Mitt. 27 (1980) 261–266.
- [38] N.W. Alcock, Acta Crystallogr. Sect. B 29 (1973) 498–502.
- [39] J.D. Grice, V. Maissonneuve, M. Leblanc, Chem. Rev. 107 (2007) 114–132.
- [40] Y. Ni, J. Hugues, A.N. Mariano, Am. Mineral. 78 (1993) 415–418.
- [41] B. Frit, M.M. Chbany, J. Inorg. Nucl. Chem. 31 (1969) 2685–2693.
- [42] H. Ma, Z. Tian, R. Xu, B. Wang, Y. Wei, L. Wang, Y. Xu, W. Zhang, L. Lin, J. Am. Chem. Soc. 130 (2008) 8120–8121.