



High temperature crystal structures and superionic properties of SrCl₂, SrBr₂, BaCl₂ and BaBr₂

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ABSTRACT

The structural properties of the binary alkaline-earth halides SrCl₂, SrBr₂, BaCl₂ and BaBr₂ have been investigated from ambient temperature up to close to their melting points, using the neutron powder diffraction technique. Fluorite-structured SrCl₂ undergoes a gradual transition to a superionic phase at 900–1100 K, characterised by an increasing concentration of anion Frenkel defects. At a temperature of 920(3) K, the tetragonal phase of SrBr₂ undergoes a first-order transition to a cubic fluorite phase. This high temperature phase shows the presence of extensive disorder within the anion sublattice, which differs from that found in superionic SrCl₂. BaCl₂ and BaBr₂ both adopt the cotunnite crystal structure under ambient conditions. BaCl₂ undergoes a first-order structural transition at 917(5) K to a disordered fluorite-structured phase. The relationship between the (disordered) crystal structures and the ionic conductivity behaviour is discussed and the influence of the size of the mobile anion on the superionic behaviour is explored.

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1. Introduction

The temperature dependence of the crystal structures of compounds of composition AX₂, where A=Ca²⁺, Sr²⁺, Ba²⁺ and Pb²⁺ and X=F⁻, Cl⁻ and Br⁻, have been extensively studied using a variety of experimental and computational techniques, with particular interest focussed on CaF₂, SrF₂, BaF₂, β-PbF₂ and SrCl₂ because, on heating, they undergo a broad transition to a superionic phase characterised by a very high anionic conductivity (comparable to the molten state, see Fig. 1a for the case of SrCl₂) [1–8]. All five compounds adopt the cubic fluorite crystal structure (space group *Fm* $\bar{3}$ *m*, Z=4, *a*~5.4–7.0 Å) in which the cations and anions are located on the 4(*a*) 0,0,0 and 8(*c*) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ sites, respectively. The ionic arrangement can be described as a face centred cubic (*f.c.c.*) array of A²⁺ cations in which the X⁻ anions sit in all the tetrahedral interstices or, as shown in Fig. 2a, as a three-dimensional arrangement of edge-sharing AX₈ cubes.

Neutron diffraction studies initially proposed that the increase in ionic conductivity of the fluorite-structured halides is associated with the formation of thermally induced anion-Frenkel defects in which the interstitial X⁻ is located in the octahedral 4(*b*) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ interstices within the *f.c.c.* A²⁺ sublattice (labelled X4 in Fig. 2b), which are the centres of the empty anion cubes in

Fig. 2a [9]. However, subsequent studies [10], including analysis of the coherent diffuse scattering collected from single crystals of CaF₂, β-PbF₂ and SrCl₂ [11], showed that these sites are not appreciably occupied within the highly conducting phase and, instead, the preferred site for the interstitial anions is in the 48(*g*) $\frac{1}{2}, y, y$, *y*~0.38 positions, which lie between the cube centre and midpoint of a cube edge (labelled X2 in Fig. 2b). The presence of these interstitials causes the two nearest neighbour anions to relax away from the interstitial into surrounding empty cubes (32(*f*) *x,x,x* sites with *x*~0.40, shown as the X3 sites in Fig. 2b), leading to the anion-Frenkel defect model shown in Fig. 2c (with the anion interstitial and relaxed nearest neighbours labelled X_I and X_R, respectively). Quasielastic neutron scattering studies indicated that these defects have a typical lifetime of ~10⁻¹² s [11], whilst their stability was determined by static energy calculations [12].

Turning to the other members of the AX₂ (A=Ca²⁺, Sr²⁺, Ba²⁺ and Pb²⁺; X=F⁻, Cl⁻ and Br⁻) family of compounds, CaCl₂ and CaBr₂ both adopt an orthorhombically distorted version of the rutile structure (space group *Pnmm*, Z=4) and undergo a continuous transition to the tetragonal rutile form (space group *P4*₂/*mnm*, Z=2) at temperatures of 508 K and 826 K, respectively [13,14]. Neither compound shows high ionic conductivity prior to melting [5]. BaCl₂, PbCl₂, BaBr₂ and PbBr₂ all adopt the orthorhombic cotunnite structure (space group *Pnma*, Z=4) under ambient conditions [15], which can be described as a hexagonal close packed (*h.c.p.*) array of A²⁺ cations with all the tetrahedral

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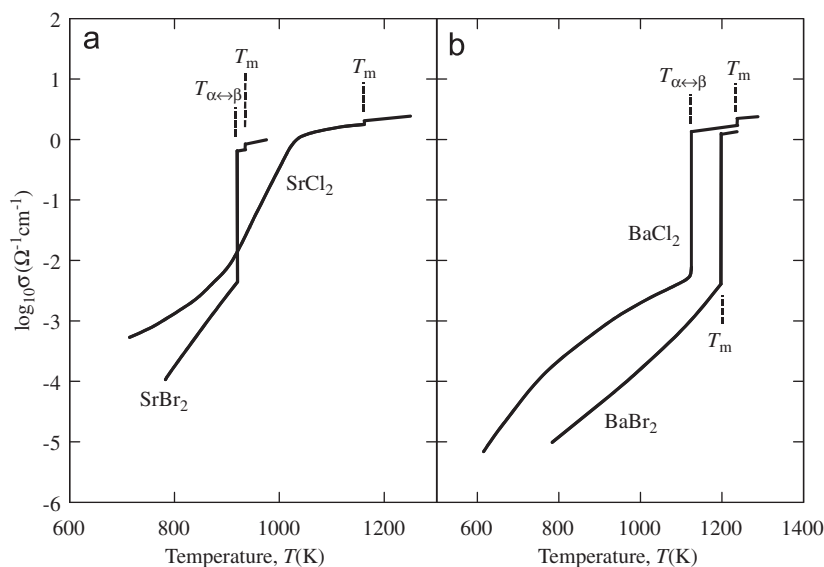


Fig. 1. The temperature dependence of the ionic conductivity, $\log_{10}\sigma$, for (a) SrCl_2 and SrBr_2 and (b) BaCl_2 and BaBr_2 (after [5,20]).

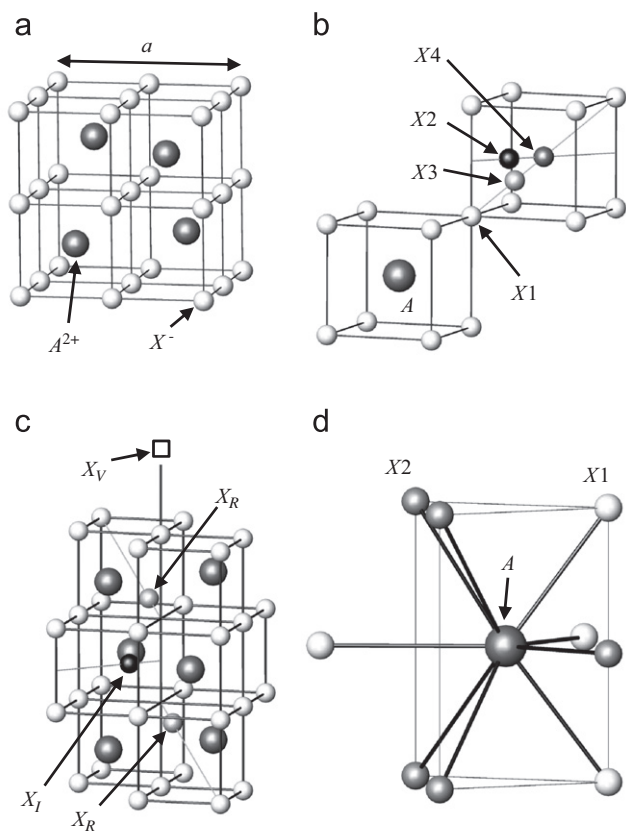


Fig. 2. (a) The cubic fluorite crystal structure of a compound of stoichiometry AX_2 , with the A^{2+} cations occupying alternate cube centres within a simple cubic array of X^- anions. The cubic lattice parameter a is shown. (b) The anion sites proposed to be occupied within anion disordered halide and oxide fluorites (after [7]). (c) The anion-Frenkel defect proposed to occur within the superionic phase of the halide fluorites [11,12]. X_V , X_I and X_R denote an anion vacancy, anion interstitial and relaxed anions, respectively. (d) The anion co-ordination surrounding a cation within a cotunnite-structured compound of stoichiometry AX_2 .

interstices occupied by two symmetry independent X^- anions. However, all the ions are displaced away from the idealised positions by significant distances, leading to a more irregular arrangement in which the A^{2+} cations are surrounded by a total of nine X^- in the form of a distorted tricapped trigonal

prism (see Fig. 2d). As a consequence of the higher co-ordination, the cotunnite structure is more densely packed than the fluorite one, and several fluorite-structured compounds transform to a cotunnite phase at elevated pressures, including BaF_2 [16], SrCl_2 [17] and PbF_2 [17–19]. In the case of PbF_2 , the cotunnite (α) form can be retained under ambient conditions, but transforms to the fluorite-structured (β) phase on heating above ~ 610 K [18]. Measurements of the ionic conductivity indicate that both BaCl_2 and PbCl_2 show high ionic conductivities in narrow temperature ranges just below their melting points (see [20] and [21], respectively, and the former is illustrated in Fig. 1b). Heat capacity measurements of BaCl_2 also show the presence of a phase transition at 1193 K, prior to melting at 1233 K [22], though no structural details have been presented for the high temperature phase.

The final compound in this family, SrBr_2 , was originally proposed to adopt the cotunnite structure on the basis of X-ray single crystal diffraction data [23]. However, this reported structure contains Sr–Br distances significantly longer than the sum of the ionic radii and led to a redetermination of the structure using X-ray powder diffraction methods [24]. SrBr_2 was shown to adopt a larger tetragonal unit cell (space group $P4/n$, $Z=10$) [25], isostructural with EuBr_2 [26] and USe_2 [27]. Drop calorimetry studies showed that SrBr_2 undergoes a solid–solid phase transition at a temperature of 918 K, prior to melting at 930 K [22], with later studies reporting temperatures of 919 K and 928 K [28] or 915 K and 922 K [29], respectively. The solid–solid transition was found to possess a higher entropy than the melting transition ($13.2\text{ J K}^{-1}\text{ mol}^{-1}$, compared to $11.3\text{ J K}^{-1}\text{ mol}^{-1}$ [22]), which implies the presence of significant disorder within the high temperature phase. This observation was supported by the subsequent report of an abrupt increase of over two orders of magnitude in the ionic conductivity of SrBr_2 at the transition (see Fig. 1a), to a value of around $1\text{ }\Omega^{-1}\text{ cm}^{-1}$ which is only slightly lower than that found above the melting point [20].

In this paper we report the results of a powder neutron diffraction study of SrCl_2 , SrBr_2 , BaCl_2 and BaBr_2 from ambient temperatures up to close to their melting points. In comparison to the other binary AX_2 halides, the structural properties of these compounds are rather poorly understood. This allows a detailed discussion of the effects of temperature on the crystal structures, including the nature of the extensive anion disorder which characterises the superionic phases of SrCl_2 , SrBr_2 and BaCl_2 in the temperature ranges immediately below their melting points

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