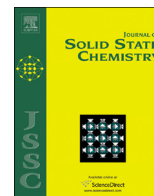




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## Solid solution barium–strontium chlorides with tunable ammonia desorption properties and superior storage capacity

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## ABSTRACT

Metal halide amines are very attractive materials for ammonia absorption and storage—applications where the practically accessible or usable gravimetric and volumetric storage densities are of critical importance. Here we present, that by combining advanced computational materials prediction with spray drying and *in situ* thermogravimetric and structural characterization, we synthesize a range of new, stable barium–strontium chloride solid solutions with superior ammonia storage densities. By tuning the barium/strontium ratio, different crystallographic phases and compositions can be obtained with different ammonia ab- and desorption properties. In particular it is shown, that in the molar range of 35–50% barium and 65–50% strontium, stable materials can be produced with a practically usable ammonia density (both volumetric and gravimetric) that is higher than any of the pure metal halides, and with a practically accessible volumetric ammonia densities in excess of 99% of liquid ammonia.

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## 1. Introduction

Metal halide amines are superior materials for ammonia/hydrogen storage and desorption with a wide range of applications including thermochemical heat pumps, ammonia separation, fuel cells and selective catalytic reduction (SCR) [1–8]. Metal halide amines in general show ammonia desorption temperatures ranging from below room temperature to above 400 °C [1]. For many applications such as e.g. fuel cells and SCR, however, a temperature range between 20 °C and 100 °C is highly desirable. The lower limit of 20 °C is set for safety reasons to reduce the toxic vapor pressure when the system is not in operation. The higher limit, 100 °C, is advantageous to (i) limit the time and energy needed to release the ammonia, (ii) enable the use of waste heat, often in the form of hot water, for desorption, and (iii) enable use of cheap engineering materials. The ammonia that desorbs between 20 °C and 100 °C at 1 bar is here defined as the usable ammonia content. In this narrow temperature window strontium and calcium chlorides are the most interesting among the pure metal halides. CaCl<sub>2</sub> binds 8 ammonia molecules, and has the highest gravimetric ammonia capacity among the metal halides (551 g NH<sub>3</sub>/kg). However, the last 2 ammonia molecules require temperatures of 198–242 °C to desorb [1]. If the temperature is

limited to 100 °C, the usable gravimetric ammonia density decreases to 413 g NH<sub>3</sub>/kg. In the same way, the gravimetric ammonia density of SrCl<sub>2</sub> decreases from 462 g NH<sub>3</sub>/kg to a usable gravimetric ammonia density of 404 g NH<sub>3</sub>/kg.

Recent studies have shown that ammonia binding energies and material densities depend on the elements and crystal structures of the salts [9]. The determination of the ammonia equilibrium pressures combined with X-ray diffraction (XRD) and density functional theory (DFT) calculations brought a complete understanding of the crystal structures of the strontium chloride amines and revealed that several different crystal structures exist with energies close to the ground state. Only small modifications are needed to interchange the energies, and thus the stability of these structures. Further, Aika and Liu showed that bromides and chlorides of strontium and calcium spontaneously form mixed solid solutions with ammonia binding properties different from the pure salts [10].

These observations led us to investigate the possibility to design novel ammonia storage materials based on mixed solid solutions of metal halides, with the target of obtaining simultaneous high usable gravimetric and volumetric ammonia density. Strontium chloride is one of the metal halides with the highest usable ammonia storage capacity. And since barium is an abundant impurity of naturally occurring strontium minerals and the only metal halide known with high ammonia density, which releases all the ammonia in one step, we chose to investigate the barium–strontium chloride system.

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## 2. Materials and methods

### 2.1. Synthesis

Solid solutions of strontium and barium chlorides were prepared by spray drying of the aqueous solutions, a method which is commonly used in production of strontium chloride. Prior to the experiment, strontium chloride and barium chloride (min. purity 99%) were dried in an oven at 200 °C. So obtained anhydrous compounds, in pre-described molar ratios, were dissolved in demineralized water to obtain a 10 wt% aqueous solution. Mixtures with stoichiometries ranging from 99:1 to 25:75, SrCl<sub>2</sub>:BaCl<sub>2</sub> were prepared. A laboratory scale B290 Buchi Mini Spray Dryer was used with the following settings: (a) inlet temperature: 220 °C, (b) feed rate: 10% (0,2 L/h), (c) aspirator rate: 60% (20 m<sup>3</sup>/h), (d) spray drying air flow: 40 mm (680 NL/h). Prior to testing all the samples were further dried in an oven at 200 °C for 24 h to reach a water content below 0.05 wt%.

### 2.2. Characterization

So prepared materials were characterized in regards to their structure, ammonia absorption and desorption properties, and densities. Structures were investigated using Powder diffraction X-ray (PXRD) and were recorded on a BRUKER D8 (40 kV, 40 mA, Cu radiation  $K\alpha=1.542 \text{ \AA}$ ). To avoid contact with air or moisture a polyethylene film covered the samples. The film gives rise to the background in the angular range from 10° to 25° in  $2\theta$ , background accompanied by two broad peaks at around 21° and 25° in  $2\theta$ . These peaks were excluded from the patterns during the Rietveld refinements. Ammonia absorption and desorption properties were analyzed using thermogravimetric desorption measurements, which were performed on a high pressure thermogravimetric analyzer, HP-TGA ISOSORP Gas LP-flow from Rubotherm. A unique feature of this instrument is the separation of the balance from the sample environment by magnetic coupling, which allows for the use of corrosive gases, such as ammonia. All samples were analyzed with the same method comprising the following steps: (a) annealing of the sample at 200 °C in nitrogen gas atmosphere, (b) cool down to 20 °C and evacuation, (c) saturation with ammonia gas at 5 bar at 20 °C, (d) desorption of ammonia by increasing temperature by 1 °C/min in 1 bar of ammonia gas. The density of ammoniated samples was measured by compacting the material under a mechanical pressure of 740 MPa (7.5 t/cm<sup>2</sup>) and measuring the density of the obtained pellets. Samples were kept cold prior to testing to avoid ammonia desorption, measurements were performed in dry nitrogen atmosphere and the ammonia content was verified after each measurement by heating and weighing the samples. Each concentration was tested three times.

### 2.3. DFT calculations

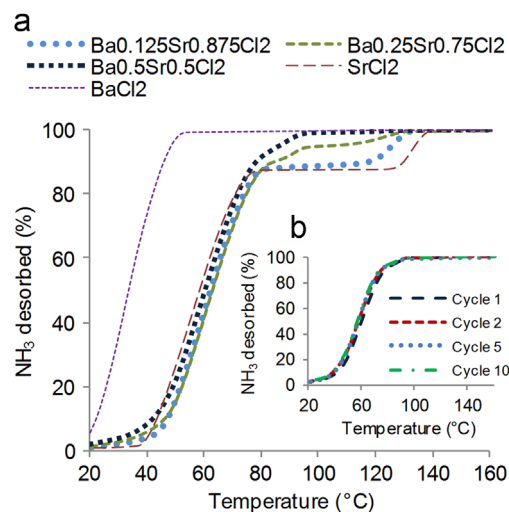
Density functional theory (DFT) calculations were performed to predict the thermodynamic and structural properties of the mixed metal halide amines, and for comparison with experimental observations. The calculations were done within the Atomic Simulation Environment (ASE) using the GPAW code; a real space implementation of the Projector Augmented Wave (PAW) method [11–15]. The vdW-DF functional was used to account for dispersion and van der Waals forces [16]. The Brillouin-zone was sampled using a Monkhorst-Pack grid with at least 25  $k$ -points per  $\text{\AA}^{-3}$  in each direction, the grid spacing was 0.18  $\text{\AA}$  and all structures were allowed to relax the atomic coordinates by a quasi-Newton type optimization algorithm [17,18]. The energy of NH<sub>3</sub>(g) was calculated by placing a molecule in a cube with a side length of 8  $\text{\AA}$ , removing the periodic boundary conditions and

using the same grid spacing as above. The enthalpies of desorption were calculated by subtracting the absolute electronic energies of the most stable structures in the desorption step and including the gas-phase energy of the released ammonia molecules. The desorption temperatures were determined by calculating the entropic and finite temperature enthalpy corrections for the strontium and barium systems, and using the weighted averages to calculate the release temperatures using the van't Hoff equation. For the solids, the correction was found by summation of the mean energies of the vibrational frequencies calculated in the harmonic approximation at finite temperatures; the gas phase correction was calculated in the ideal gas approximation, by including the translational, rotational and vibrational degrees of freedom in the NH<sub>3</sub> molecule [19].

## 3. Results and discussion

Examples of ammonia desorption into 1 bar of ammonia when the temperature is ramped 1 °C/min from 20 °C to 160 °C from 3 different mixtures of Ba<sub>x</sub>Sr<sub>(1-x)</sub>(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub> ( $x=0.125$ ,  $x=0.25$  and  $x=0.5$ ) are shown in Fig. 1a together with Ba(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub> and Sr(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>.

For pure Sr(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>, the ammonia desorption is seen to start close to 40 °C and releases 87.5% in one step. This corresponds to 7 out of the 8 ammonia molecules. The last molecule, however, only desorbs above 125 °C. For pure Ba(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>, all 8 ammonia molecules are desorbed below 50 °C. When barium is added to Sr(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>, the desorption of the first 7 molecules resembles desorption from pure Sr(NH<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>. The effect of the increasing barium concentration is mostly a shift in desorption of the last ammonia molecule to lower temperatures. For the composition Ba<sub>0.5</sub>Sr<sub>0.5</sub>Cl<sub>2</sub>, essentially all the ammonia desorbs in one step and results in a usable gravimetric ammonia density of 422 g NH<sub>3</sub>/kg. This excellent behavior is maintained with cycling as seen in Fig. 1b: Ba<sub>0.5</sub>Sr<sub>0.5</sub>Cl<sub>2</sub> is saturated with ammonia and degassed 10 times in total. A small change is observed from the first to the second cycle. This is seen in all cycling experiments for pure and mixed salts, and is associated with formation of porosity in the first cycle [8]. Apart from that, the amount of ammonia desorbing below 100 °C remains constant (Fig. 1b) and no degradation is observed. The stability was confirmed by XRD. Fig. 2 presents the diffraction patterns of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Cl<sub>2</sub> before and after seven



**Fig. 1.** Ammonia temperature programmed desorption (TPD) curves. (a) Ammonia TPD from Ba<sub>x</sub>Sr<sub>(1-x)</sub>Cl<sub>2</sub> with  $x$  equal to 0.125, 0.25 and 0.5. (b) Ammonia TPD from Ba<sub>0.5</sub>Sr<sub>0.5</sub>Cl<sub>2</sub> after 1, 2, 5 and 10 saturation cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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