Flame synthesis of calcium-, strontium-, barium fluoride nanoparticles and sodium chloride

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Received (in Cambridge, UK) 21st December 2004, Accepted 21st January 2005
First published as an Advance Article on the web 3rd February 2005
DOI: 10.1039/b419099h

Non-oxidic salts such as NaCl, CaF_2, SrF_2 and BaF_2 were synthesised using a flame spray method; optional doping of such fluorides with rare earth elements suggests possible applications in optics.

The current need for computer power has pushed chip manufacturing to UV-applications using 193 and 154 nm lithography. A major hurdle towards such large scale applications is the cost effective production of high purity fluoride crystals and glasses.[1a] Current fibre optics rely on doped silica that is manufactured in a flame process[1b] for its inherently low entrainment of impurities. Such impurities result in scattering centers and signal loss upon transmission. The present work describes a method to prepare metal salts, especially halides by a similar flame process and extends the similar, yet existing technology to this novel material class. Among the different halide salts, mainly fluorides have wide applications in optics as windows, lenses, scintillation crystals[1c] and as host crystals for rare earth ions (Ho, Er, Eu, Nd, Ce) exhibiting interesting properties in optoelectronics such as lasing,[1d] light amplification and upconversion.[1e,2a,b] Fluoride-based fibre optics may be obtained from doped ZrF_4 and BaF_2 based glasses.[2c,d]

Iksue *et al.*[3a] have shown that polycrystalline structures with crystal sizes in the nanometer regime show very high transparency and optical properties similar to single crystals for laser applications. Currently nano-crystalline salts can be produced by liquid phase methods using microemulsions.[3b–d] They are limited to very low concentrations and often suffer from the uptake of impurities or remaining surfactants. Flame synthesis of inorganic materials has rapidly evolved during the past years:[4a] Starting from the preparation of mixed oxides for catalysis,[4b–d] more complex materials such as doped apatites,[4e] carbonates[4f] or yttrium–aluminium–garnet[4g] have become accessible by a continuous, dry, gas-phase process. Here we want to extend the present products from flame synthesis to metal fluorides and chlorides.

Alkaline earth fluorides and sodium chloride were produced by mixing corresponding metal 2-ethylhexanoate liquid precursors[4i–k] with stochiometric amounts of a fluoro- or chlorobenzene and spraying the resulting liquid into a methane–oxygen-flame.[4h] The product powder was collected on a preheated filter plate to avoid the condensation of water. Neither the off-gas nor the product contained any measurable amounts of acids (HF or HCl). Experiments were performed using either calcium, strontium or barium 2-ethylhexanoate together with hexafluorobenzene, resulting in CaF_2, SrF_2 and BaF_2, respectively. Sodium 2-ethylhexanoate and chlorobenzene resulted in ordinary stone salt (NaCl) particles of high purity, as demonstrated by dissolving the product in water and measuring the resulting pH that remained neutral. To illustrate the feasibility of rare earth incorporation into fluorides a sample of BaF_2 doped with 1at% Ho was prepared using a precursor containing barium 2-ethylhexanoate with 1at% holmium 2-ethylhexanoate and a stochiometric amount of hexafluorobenzene.

The produced powders consist of nanoparticles with diameters of 20 nm for CaF_2 to well above 100 nm for NaCl, which is consistent with nitrogen adsorption measurements (BET, see Table 1) and peak width from X-ray diffraction patterns (Fig. 1) calculated using the Scherrer formula. Transmission electron microscopy (TEM) of the fluorides (Fig. 2) shows regularly shaped cubic crystallites for BaF_2 and slightly irregular spheroid nanoparticles for SrF_2 and CaF_2. When switching from CaF_2 to SrF_2 or BaF_2 an increase of the primary particle size can be observed together with a decrease of the degree of agglomeration. Scanning electron microscopy (SEM) of sodium chloride (Fig. 3)

Table 1 Products synthesised by flame spray pyrolysis

M in metal 2- ethylhexanoate	Halide Source	Product	Surface area[a]/m^2g^{-1}	d_p[b]/nm
Ca	C_6F_6	CaF_2	139	14
Sr	C_6F_6	SrF_2	84	17
Ba	C_6F_6	BaF_2	36	34
Na	C_6H_5Cl	NaCl	30	92
Ba + 1at% Ho	C_6F_6	Ho–BaF_2	48	26

[a] Measured by nitrogen adsorption; errors ±3%. [b] Calculated primary particle diameter assuming spherical particles.

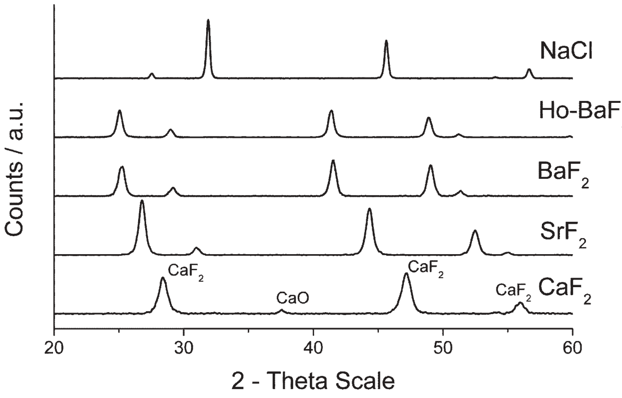

Fig. 1 X-ray diffraction patterns of the as-synthesised salts. Only the CaF_2 pattern contains peaks from calcium oxide impurities.

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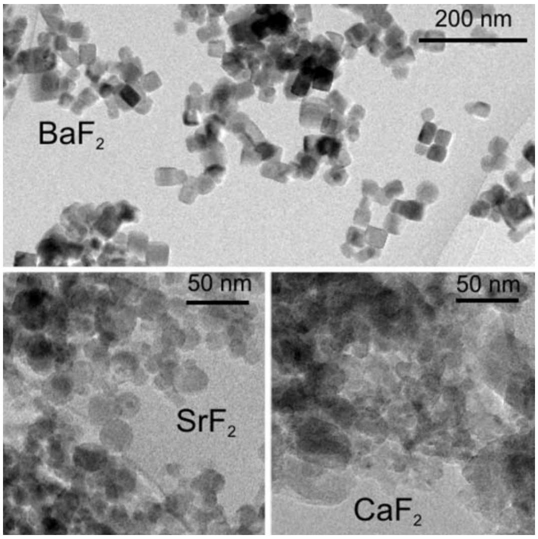

Fig. 2 Transmission electron micrograph of flame-made alkaline earth fluorides. The powders show high crystallinity and low agglomeration in the case of BaF_2.

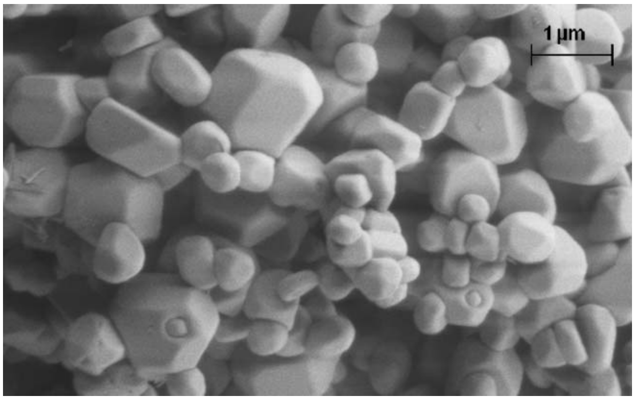

Fig. 3 Scanning electron micrograph of flame-made NaCl. Irregular crystallites of a wide size range are visible.

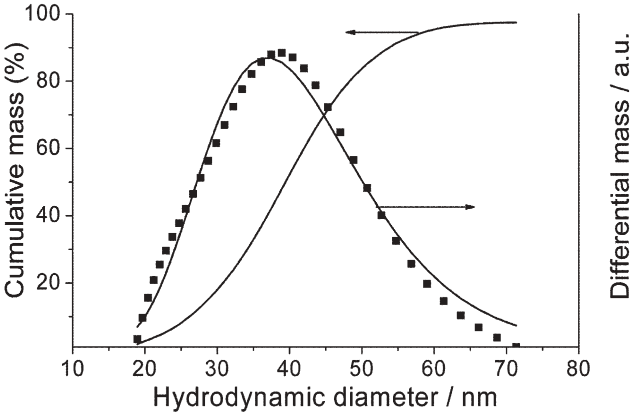

Fig. 4 Cumulative and differential particle size distribution of the BaF_2 dispersed in ethylene glycol, measured by X-ray disc centrifuge. The dotted line shows the best log normal fit to the data with a geometric standard deviation of 1.33 consistent with theoretical calculations.[5b,c]

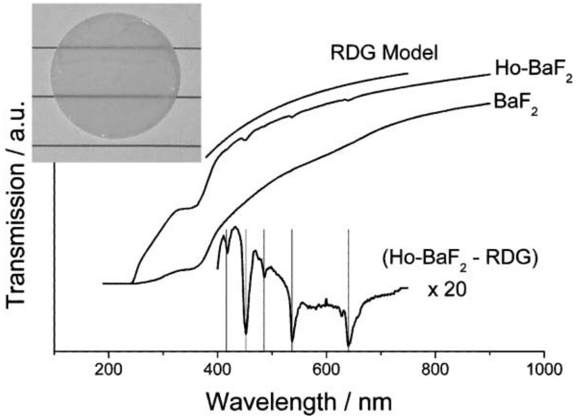

Fig. 5 UV-VIS transmission spectra of BaF_2 and Ho–BaF_2. RDG represents the best fit according to the Rayleigh–Debye–Gans model. The bottom line represents the subtraction of the measured data from the model giving the holmium spectrum. Vertical lines show the expected absorption peaks according to Travis *et al.*.[5e] Inset: Photograph of a BaF_2 pill (1.3 cm diameter).

shows a much broader particle size distribution as well as larger particles. The latter may result from grain growth due to moisture as observed by Sata.[5a]

X-ray diffraction (XRD) analysis (Fig. 1) shows high crystallinity for all products. While the CaF_2 diffraction pattern shows small contributions of CaO, the other diffraction patterns indicate the absence of oxidic species. For holmium doped BaF_2 no additional signals arising from inhomogenities could be observed and corroborate a good holmium incorporation.

Particle size analysis by X-ray disc centrifuge (XDC) of BaF_2 powder dispersed in ethylene glycol after short sonication is shown in Fig. 4. The particle size distribution can be described as log normal with a geometric standard deviation of 1.33, which is consistent with free molecular regime, diffusion-limited coagulation of non-fractal particles.[5b,c]

The BaF_2 powder could be formed into an optically transparent pill (Fig. 5) when pressed uniaxially for 5 min at 370 MPa at room temperature. During the compaction the specific surface area decreased to 28 $m^2\ g^{-1}$, equivalent to an increase in mean particle diameter of 10 nm. The optical properties of the pill as well as a pill pressed from the holmium doped BaF_2 powder were analysed using transmission UV-VIS spectroscopy. Fig. 5 shows the corresponding transmission spectra of the two pills. The transmission decay with the reciprocal wavelength can be accredited to light scattering. The loss in transmission can be explained according to the Rayleigh–Debye–Gans (RDG) theory[5d] as

$$T = (1 - R_s)\exp\left(-\frac{C}{\lambda^2}\right),$$

where R_s accounts for the reflection losses at the two sample surfaces, λ is the wavelength and C is a constant containing the sample thickness, the difference in refractive index and the particle radius. The constants C and R_s could be fitted to the Ho–BaF_2 line from 400 to 780 nm and then subtracted from the measured data resulting in the holmium absorbance spectrum with main peaks at 640, 536, 485, 452 and 416 nm.[5e]

The present work shows that beyond metal oxides, phosphates and carbonates even oxygen-free metal salts such as fluorides and chlorides can be formed by flame synthesis using carboxylate precursors and a suitable halide anion source. The high affinity of fluorine and chlorine towards alkali and alkaline earth metals promotes the rapid formation of the corresponding salts and suppresses oxide formation. With optional rare earth metal doping such products may find applications in optical fibre manufacture for UV-VIS applications and lasing materials.†

We thank Dr F. Krumeich for electron microscopy imaging and U. Krebs, C. Furrer and H.-P. Schläpfer for reactor construction. This work has been supported by the CTI grant Nr. 7103.1 NMS-NM.

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Notes and references

† The precursors were prepared by dissolving calcium hydroxide (Riedel-de-Haen, p.a.), strontium acetate (ABCR), barium acetate (Strem, 99%), sodium hydrogencarbonate (Merck, p.a.) and holmium oxide (Fluka, 99.9%) in 2-ethylhexanoic acid (Soctec, tech). Hexafluorobenzene (Lancaster, 99%) or chlorobenzene (Fluka, 98%) was added in a stoichiometric amount and mixed with 50 vol% xylene (Fluka, 97%). The liquid mixtures were fed through a capillary (diameter 0.4 mm) into a methane (1.13 l min^{-1}, Pan Gas, tech)/oxygen (2.4 l min^{-1} Pan Gas, tech) flame using a gear-ring pump (HNP Mikrosysteme) at a rate of 5 ml min^{-1}. Oxygen (5 l min^{-1}, Pan Gas, tech, constant pressure drop at the capillary tip 1.5 bar) was used to disperse the liquid leaving the capillary. A stable combustion was achieved by applying a sheath gas (oxygen, 230 l h^{-1}, Pan Gas, tech) through a concentric sinter metal ring.[4h] Calibrated mass flow controllers (Brooks) were used to monitor gas flows. The as-formed particles were collected on a glass fibre filter (Whatmann GF/A, 25.7 cm in diameter), placed on a cylinder mounted above the flame, by the aid of a vacuum pump (Busch). For analysis, BET measurements were performed on a Micromeritics Tristar. X-ray diffraction was conducted on a Siemens powder X-ray diffractometer using Ni-filtered CuK$_\alpha$ radiation in step mode with a step size of 0.3°. Transmission electron microscopy images were recorded on a CM30 ST (Philips, LaB$_6$ cathode, operated at 300 kV, point resolution $\sim$4 Å). Particles were deposited onto a carbon foil supported grid. UV-Vis measurements were performed using a Shimadzu UV-1650PC spectrometer in transmission mode. A Brookhaven Instruments X-ray disc centrifuge was used for particle size distribution analysis.

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