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Combinatorial hydrothermal synthesis and characterisation of perovskites

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Abstract

In the present work we have applied combinatorial methodology to the hydrothermal synthesis and characterisation of perovskites. In a first series with 48 samples in the $(Pb,Ba,Sr)ZrO_3$ compositional field, synthesis conditions were optimised by variation of pH. In a second series of 96 samples the $(Pb,Ba)(Zr,Ti)O_3$ compositional field was investigated, with the aim to control crystallinity and particle size. Using powder X-ray diffraction (XRD), it was established that most compositions crystallised readily within 3–23 h at 200 °C in 2.0–3.3 M KOH. Using scanning electron microscopy (SEM), particle size was determined to be from 3 to 8 μm for the pure zirconates to 0.2–1 μm for the pure titanates. Microprobe wavelength dispersive spectroscopy (WDS) was used for chemical analysis. It was found that particle size was determined primarily by bulk chemistry whereas a polyacrylamide additive and pH had little effect. It has been shown that combinatorial hydrothermal synthesis and characterisation techniques are fully applicable to the synthesis and basic characterisation of perovskites.

Keywords: Perovskites; Combinatorial; Powders-chemical preparation; Grain size; Hydrothermal methods

1. Introduction

Combinatorial methods are well-suited for preliminary screening of multi-parameter spaces, typically where complex compositions are desired. Briceno et al.[1] synthesised arrays of oxides, including perovskites using combinatorial thin film deposition and physical masking techniques, and Reichenbach and McGinn[2] synthesised arrays of perovskites applying a polymerisable complex method. At SINTEF, combinatorial hydrothermal techniques were originally developed for the synthesis of zeolites.[3] The system built around our *MultiAutoclave*[4] has been extended and refined to various applications within the field of catalysis.[5–6]

Perovskite and materials with a perovskite-like structure can be described by the general formula ABO_3. In the following, these materials will be referred to as perovskites. Many perovskites have useful electronic properties. Among these are lead zirconate titanate (PZT) which is a piezoelectric material of commercial importance,[7–8] and barium titanate (BT) which has useful dielectric and ferroelectric properties.[9]

Perovskites can be prepared by a variety of methods such as the much used sol–gel-, complexation- (e.g. citric acid), hydrothermal-, and conventional ceramic synthesis methods. The advantages of hydrothermal synthesis as compared to other methods are that fine powders with tuneable particle size and uniform morphology with good sintering properties, low contamination by impurities and controlled agglomeration can be obtained.[7–12] For example, within the family of perovskites formed with Ba, Sr and Pb as A-ion and Ti and Zr as B-ions hydrothermal synthesis of perovskites have been reported for $BaTiO_3$,[13–17] $PbTiO_3$,[10,18,19] $SrZrO_3$,[14] and the solid solution series $PbZr_xTi_{1-x}O_3$,[7,8,20–25] $BaZr_xTi_{1-x}O_3$[11] and $Pb_xBa_{1-x}TiO_3$.[9]

Important parameters in hydrothermal synthesis of perovskites are pH, reaction time, temperature and the presence of additives. pH must be within a certain range for certain phases or compositions to form, and will also often affect particle size.[7,10] The presence of salts may hamper the substitution of elements into the structure, and may hinder complete crystallisation.[7]

In combinatorial preliminary screenings, the ambition is to rapidly obtain indications to promising candidates for

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further focused work. The aim of the present work has primarily been to implement our combinatorial techniques to the hydrothermal synthesis of a broad range of perovskites, and to demonstrate the breadth of information that can be extracted from combinatorial basic characterisation. We have chosen to target perovskites with Pb, Ba and Sr as A-ions and Zr and Ti as B-ions. A further aim has been to manipulate the particle size of the products.

2. Experimental

2.1. Hydrothermal synthesis

The hydrothermal synthesis procedures was based on our combinatorial approach[3,4] which has now been based on a standardised format. Forty-eight syntheses are carried out in parallel using Teflon sample holders having volumes of about 2 ml. In-house developed software[26] based on LabVIEW is used to control instrumentation, and to monitor and log all relevant data during the entire process. Synthesis parameters such as reagents, temperature, synthesis time, pH and additives were chosen with basis primarily in the works of Sato et al.[10] and Vivekanandan et al.[11] with the aim to verify our methodology with reference to their results.

1.5 M aqueous solutions of $TiOCl_2$ and $ZrOCl_2$ were prepared from $TiCl_4$ (Aldrich) and $ZrOCl_2$ (Fluka, ≥99%). The $TiOCl_2$ was freshly prepared. 1.0 M solutions of Pb, Ba, and Sr were prepared from $BaCl_2$ (Aldrich, 99%), $Pb(NO_3)_2$ (Aldrich, 99+%) and $Sr(NO_3)_2$ (Merck, p.a.). KOH (Merck, p.a.) was used as a 10 M solution and Polyacrylamide (PAAm) with molecular weight of about 10,000 (Aldrich, 50% aqueous solution) diluted to 0.9 wt.% was used. The various reagents were added in the form of liquid solutions by means of a Zinsser Lissy pipetting robot, while the mixtures were simultaneously shaken. Good mixing was aided by presence of steel beads in the mixtures. Mixtures were transferred to the MultiAutoclave,[4] which was heat treated under autogeneous pressures at 200 °C.

In a first experimental series (series 1), eight different combinations of Pb, Ba and Sr as A-ions and Zr as B-ion in the eight compositional relations were prepared: Pb–Zr, (0.67Pb–0.33Ba)–Zr, (0.33Pb–0.67Ba)–Zr, Ba–Zr, (0.67Ba–0.33Sr)–Zr, (0.33Ba–0.67Sr)–Zr, Sr–Zr, and (0.33Pb–0.33Ba–0.33Sr)–Zr. These were repeated in each of the six rows of 8 in the 48 sample array. The corresponding product groups will be referred to as PZ-1, $(P_{2/3}B_{1/3})$Z-1, $(P_{1/3}B_{2/3})$Z-1, BZ-1, $(B_{2/3}S_{1/3})$Z-1, $(B_{1/3}S_{2/3})$Z-1, SZ-1 and $(P_{1/3}B_{1/3}S_{1/3})$Z-1, respectively, even if the real composition may deviate from the target composition. When individual samples are referred to, the cell reference will be added as, e.g. PZ-1 (A1). pH was varied by the addition of KOH to final concentrations of 1.0, 2.0 and 3.0 M KOH in pairs of rows. The resulting 24 compositions were prepared with and without a small amount of La (3% atomic relative to A-ions) in every second row, and the altogether 48 batches were crystallised at 200 °C for 6 h in the MultiAutoclave[4] (at autogeneous pressure). This time includes the time of heating up, which is about 1 h, before set temperature is reached.

In the second experimental series (series 2), A-ions Sr and La were excluded and another B-ion, Ti, and an additive, polyacrylamide (PAAm) was included. KOH concentrations of 2.0 M, 2.7 M, and 3.3 M were used. Two identical arrays with 48 batches in each were prepared, one was crystallised for 3 h and the other for 23 h at 200 °C, again including the heating up time of about 1 h. Eight different compositions on A- and B-ion reagent basis, Pb–Zr, (0.5Pb–0.5Ba)–Zr, Ba–Zr, Pb–Ti, (0.5Pb–0.5Ba)-Ti, Ba–Ti, Pb–(0.5Zr–0.5Ti), and Ba–(0.5Zr–0.5Ti) were prepared, with batch compositions as given in Table 1. The corresponding compositional product groups will in the following be referred to as PZ-2, $(P_{1/2}B_{1/2})$Z-2, BZ-2, PT-2, $(P_{1/2}B_{1/2})$T-2, BT-2, $P(Z_{1/2}T_{1/2})$-2, and $B(Z_{1/2}T_{1/2})$-2, respectively.

When necessary, "−2", and "/3 h" or "/23 h" will be added to distinguish samples of series 2 from series 1, and samples crystallised for 3 h and 23 h, respectively. Also, when addressing individual samples, the cell reference will be added as, e.g. PZ-2/23 h (A1).

After cooling, the solid products for the two series were transferred to a washing unit and washed five times with distilled water between cycles of centrifugation. The washed products were dried at 110 °C, and subsequently gently crushed before sample preparation for analysis.

2.2. Characterisation

Phase content analyses were based on powder X-ray-diffraction (XRD) data collected on a Bruker D8 Discovery diffractometer with Cu $K\alpha_{1,2}$-radiation. The diffractometer is equipped with Göbel mirror, general analysis diffraction detector system (GADDS), and an xyz-stage whereby 48 samples in one sample holder were analysed in each run. Each sample was run for 2 min covering the range 24–56° 2 theta in order to obtain an XRD-pattern of acceptable quality for phase identification. Scanning electron microscopy (SEM) analyses were run on a JEOL 5900LV equipped with an xyz-stage in the sample chamber. All samples were imaged in automated set-up screen-mode at a magnification of 2000×. At this magnification the autofocus and auto brightness functions could be used, but it was found advantageous to carry out manual adjustments on the first sample on each array. With this procedure, moving to, and imaging of one sample took about 2 min only.

Chemical analyses were done by wavelength dispersive spectroscopy (WDS) using a Cameca SX 100 microprobe, also equipped with a xyz-stage, allowing semi-automated operation. For "bulk" analysis, three 50 × 50 μm spots on each sample were analysed and averaged, with an uncertainty within ±2% relative. The penetration depth is 1–1.5 μm for the compositions analysed in the present work. The results were normalised to 100% for the sum of the six elements Ba,