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Assay measurements of oxide materials by thermogravimetry and ICP-OES

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Abstract

Purity data for inorganic chemicals are usually on metals basis. A high nominal purity does not guarantee that the material has the theoretical assay value. Deviations range from some tenth % ($CaCO_3$) up to ≈10% (La_2O_3) for commercial chemicals with nominal 99.999% purity. In critical cases, ICP-OES and/or TG measurements provide good ways to obtain quantitative assay data and to define conditions that lead to the desired results of synthesis processes as crystal growth.

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Keywords: Oxides; Carbonates; Thermogravimetry; ICP-OES; Assay

1. Introduction

Often high-purity (usually at least 99.99%) starting materials are mixed in a well defined ratio for the production of certain materials as functional ceramics or crystals. Deviations from the desired stoichiometry are critical especially for the growth from the melt of single crystals $A_{m\pm\delta}B_n$ with finite homogeneity range $\delta(T)$. Inclusion-free crystals can usually only be obtained from melts with that singular composition where the solidus of the crystal and the liquidus have their joint maximum at the melting point T_f of the congruent composition. Moreover it is required, that this composition is within the homogeneity range for all $T < T_f$. Maintaining the desired ratio of mixture for two or more substances seems to be easy; but in fact it is not so straightforward in some cases.

Some chemical elements have one or more oxides that are stable or metastable under ambient conditions ($\vartheta \approx 25\,^\circ C$, oxygen fugacity $p_{O_2} = 0.21\,bar$, humidity expressed as $p_{H_2O} \approx 1–10\,mbar$, carbon dioxide fugacity $p_{CO_2} \approx 3 \times 10^{-4}\,bar$). Such oxides are often good starting materials for crystal growth. Traces of moisture that might be adsorbed to the oxide powder can be removed by annealing at $\vartheta \gg 100\,^\circ C$ if the oxide is stable at elevated temperatures. Unfortunately, some oxides are known to react very quickly with ambient humidity or carbon dioxide (e.g. of alkaline metals or earth alkaline metals). In such cases other compounds (e.g. carbonates) must be used to ensure quantitative assay of the corresponding element.

This paper presents investigations on the real chemical composition of some nominally “pure” substances commonly used for the growth of oxide crystals. The assay measurements were performed directly with inductively coupled plasma-optical emission spectroscopy (ICP-OES) and indirectly by the determination of TG steps during heating.

2. Experimental

Thermoanalytic measurements were performed with NETZSCH STA 409C (DTA/TG) or STA 449C “Jupiter” (DSC/TG) analyzers. Usually, the simultaneous DTA/TG or DSC/TG mode was used. Occasionally, the TG only measurement mode with larger TG crucibles allowed a reduction of the experimental error. Standard crucibles made of Al_2O_3 are well suited for measurements with pure solids. If not mentioned otherwise, the measurements were performed

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with heating/cooling rates of ±10 K/min in flowing argon (99.999%, 20–50 ml/min). ICP-OES measurements compare the intensity of spectral lines obtained from the sample with the intensity of lines from calibrated standards. After careful calibration, main components as well as trace impurities down to $\ll$1 ppm can be measured quantitatively with high precision. For the present study a “IRIS Intrepid HR Duo” (Thermo Elemental, USA) was used. The precision is ≈3% relative standard deviation (R.S.D.) for concentrations above background equivalent concentration (BEC).

3. Results and discussion

3.1. Decomposition of carbonates: calcium, strontium, barium, lithium

Calcium carbonate $CaCO_3$ is a standard starting material for the growth of oxide crystals with Ca as component. Oxide borates with the general formula $LnCa_4O(BO_3)_3$ (Ln = lanthanide element or yttrium) are one example. The monoclinic crystals are noncentrosymmetric and show nonlinear effects as second harmonic generation. “LnCOB” crystals can be grown from melts within the partial triangle $Ca_3(BO_3)_2$–$Y_2Ca_3(BO_3)_4$–Y_2O_3 of the ternary system CaO–B_2O_3–Y_2O_3 [1,2]. Vivien et al. [3] reported that $GdCa_4O(BO_3)_3$ single could be grown from melts that are either stoichiometric (CaO:Gd_2O_3:B_2O_3 = 8:1:3) or that have a slight CaO deficit. On the other hand, the composition of different crystals was measured by ICP and was found to be always identical to the stoichiometry. These observations suggest that the starting material $CaCO_3$ might have an increased Ca assay. Indeed, ICP-OES analysis of nominally pure (>99.99%) $CaCO_3$ from different suppliers resulted always in Ca assays that are by some 0.1% higher than the theoretical 40.04% (corresponds to 56.04% on the basis CaO). The question is, where the excess CaO could come from?

From the lime-burning reaction

$$CaCO_3 \rightleftarrows CaO + CO_2 \qquad (1)$$

one calculates a theoretical mass loss of 43.97%. Fig. 1 shows, that the $CaCO_3$ decomposition starting at ≈600 °C yields a slightly smaller TG step of 43.73%. Additionally, a smaller TG step (0.12%) was observed at 350–400 °C. A second heating run immediately after this first one did not show any significant TG effects.

Immediately after the second run a small drop of water was added to the TG sample. One can expect the quick formation of calcium hydroxide

$$CaO + H_2O \rightleftarrows Ca(OH)_2 \qquad (2)$$

from the CaO that was formed during thermolysis (1). Excess water was removed from the powder by pumping the sample inside the DSC/TG apparatus with a turbo molecular pump for 1 h down to 0.06 Pa. The dashed line in Fig. 1 shows the result of a subsequent TG measurement in flowing argon: A large TG step of ≈19% is observed in the same ϑ range like the small TG step in the first run with $CaCO_3$. One can conclude, that the decomposition of $Ca(OH)_2$ impurities contained in the nominally 99.999% pure $CaCO_3$ is responsible for the 0.12% TG step and for the excess CaO assay, as the thermolysis of calcium hydroxide (back reaction of (2)) results in a mass loss of only 24.32% being considerably smaller than the mass loss of $CaCO_3$.

The total amount of both components can be calculated from the corresponding TG signals: $CaCO_3 : 43.73/43.97 \times 100\% = 99.45\%$. $Ca(OH)_2 : 0.12/24.32 \times 100\% = 0.49\%$. Both values sum up to 99.94%. The measured TG onset temperatures are in fairly good agreement with thermodynamic equilibrium calculations with FactSage [4]. Such calculations show, that the decomposition of $Ca(OH)_2$ has to be expected in the range $\vartheta \approx 300$–$400\,^\circ C$. $CaCO_3$ should decompose in the range $\vartheta \approx 600$–$700\,^\circ C$. The slight shift of the experimental curves (Fig. 1) to higher ϑ is probably due to the neglect of kinetic effects by the equilibrium calculation.

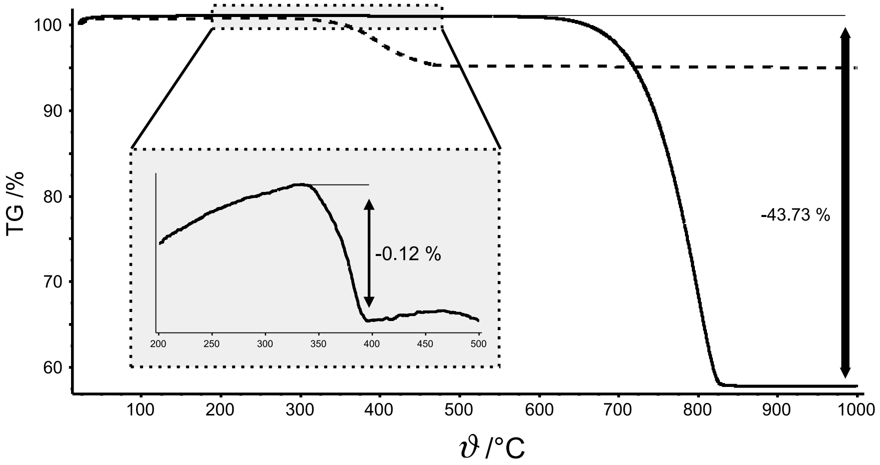

Fig. 1. Solid line and insert: TG of 136.39 mg $CaCO_3$ (Alfa Aesar 99.999%, pre-dried at 140 °C) in argon (40 ml/min). Dashed line: TG of $Ca(OH)_2$ obtained from the thermolysis product and water.

Lithium carbonate, Li_2CO_3, is the common starting material for many lithium containing oxide crystals. Lithium niobate, $LiNbO_3$, is the most important example. The excellent non-linear properties of $LiNbO_3$ crystals ensure permanent interest for this material, e.g. for holographic data storage [5]. Unfortunately, the stoichiometric composition $x_{Li} = 0.500$ with superior non-linear properties is different from the congruently melting composition with $x_{Li} = 0.486$ [6]. Some other crystals as $LiTaO_3$, $LiGaO_2$, $LiAlO_2$, or $CsLiB_6O_{10}$ are made from Li_2CO_3 as starting material too. The thermolysis reaction

$$Li_2CO_3 \rightleftarrows Li_2O + CO_2 \uparrow \tag{3}$$

proceeds with a theoretical mass loss due to CO_2 emanation of $(\Delta m/m)_{theor} = 59.56\%$.

Thermodynamic equilibrium calculations with FactSage show, that the thermolysis of Li_2CO_3 starts at 600–700 °C. De Forcrand reported almost one century ago, that the decomposition of the substance is usually incomplete at medium temperatures and that the decomposition is accompanied by a partial vaporization of Li_2O at higher ϑ [7]. The experimental TG curve (dashed line in Fig. 2) shows, that the decomposition is indeed not yet completed at 1200 °C. Even heating up to 1550 °C did not lead to a complete decomposition. Otherwise, complete decomposition of Li_2CO_3 at 780–800 °C can be obtained under flowing hydrogen [7].

For the production of powdered $LiNbO_3$ starting material for crystal growth a powdered mixture of Li_2CO_3 and Nb_2O_5 is annealed. CO_2 evolution from this mixture is finished already by heating to 720 °C [8]. Instead of Nb_2O_5 (with not well-defined oxygen content) dried $A1_2O_3$ (99.999% purity) was added in excess to the lithium carbonate in the present study. The formation of different lithium aluminates accelerates the CO_2 formation considerably; the reaction is finished already at $\vartheta < 1200\,°C$.

The TG step height in Fig. 2 $(\Delta m/m)_{exp} = 59.57\%$ is almost in coincidence with the theoretical value $(\Delta m/m)_{theor}$ expected from (3) and indicates, that the sample is free of impurities.

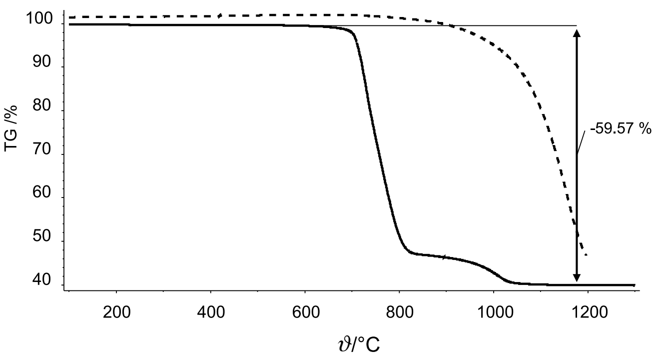

Fig. 2. Dashed line: TG of 100.22 mg Li_2CO_3 (Merck suprapur, not pre-dried) in argon (40 ml/min). Solid line: TG of a mixture (21.73 mg Li_2CO_3 Merck suprapur +50.66 mg Al_2O_3 Auer Remy 5N). Mass scaling always for the Li_2CO_3 content.

Ferroelectric $Sr_{1-x}Ba_xNb_2O_6$ (SBN, [9]) and some other crystals are usually made of the corresponding alkaline earth carbonates as one starting material. $SrCO_3$ and $BaCO_3$ decompose with theoretical mass losses of 29.81 or 22.30%, respectively, at heating. The TG steps of measurements in argon are more smeared out as for $CaCO_3$; therefore the exact determination of their heights is difficult. The thermolysis can be accelerated considerably, if the measurement is performed in vacuum.

Under vacuum conditions of a turbo molecular pump some unexpected effects can be observed: If larger amounts of gaseous species (CO_2 in the present case) are released from the sample, the mass seems to rise, as the emanating gas molecules transfer impulse to the sample holder. Not until the complete gas is released, this effects disappears and the balance reaches equilibrium. Moreover, a general drift of the TG curve can be observed under high vacuum, as the mean free path of molecules exceeds the dimensions of the DSC furnace. Therefore a correction measurement is inevitable. The solid line in Fig. 3 represents the difference between a first measurement with fresh $SrCO_3$ and a subsequent measurement with the decomposition product SrO immediately afterward. The measured mass loss (29.78%) is in very good agreement with the theoretical one (29.81%), indicating that the material contains no volatile impurities. The same result was obtained with $BaCO_3$ samples from different suppliers: The measured TG steps were always within ±0.1% in agreement with the theoretical value 22.30%.

3.2. Oxides and other compounds: lanthanum, magnesium and iron

If available, stable oxides are the preferred starting materials for the production of oxide materials. If only one valency state is known to be stable, annealing in air is often a good way to remove volatile impurities. The reaction of some rare earth oxides, especially La_2O_3, with moisture is well known for a long time but sometimes forgotten. Gmelin [10] reports, that at 95 °C and 95% relative humidity this oxide absorbs after 40 h as much as 3 mol H_2O per mol La_2O_3.

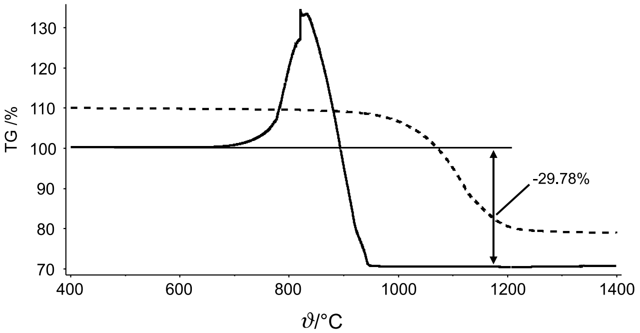

Fig. 3. Dashed line: TG of 34.79 mg $SrCO_3$ (Merck puratronic, not pre-dried) in argon (40 ml/min, curve shifted by +10%). Solid line: TG of 44.13 mg $SrCO_3$ Merck puratronic in vacuum ($p \approx 0.06$ Pa, corrected data).

In this study La_2O_3 (Meldform 99.999%) was found to loose during TG measurements in flowing argon 7.44% mass mainly in 2 TG steps with inflection points (= maximum mass loss per time unit) at 358 °C and 512 °C, respectively. The mass loss levels out at $\gtrapprox$800 °C. The high stability of $La_2(CO_3)_3$ and of the dioxycarbonate $La_2O_2CO_3$ is responsible for the high release temperature of volatiles from lanthanum oxide and from some other rare earth oxides [11]. From the TG data one calculates an experimental La assay $[\mathrm{La}]^{\mathrm{TG}} = 78.92\%$. By ICP-OES values ranging from $[\mathrm{La}]^{\mathrm{ICP}} = 76.69$ to $79.73 \pm 0.06\%$ were found for different batches. These measured data are considerably smaller than the theoretical value $[\mathrm{La}]^{\mathrm{theo}} = 85.27\%$.

Forsterite, Mg_2SiO_4, melts congruently and crystals can be grown from 2:1 molar mixtures of MgO and SiO_2. It was found by ICP-OES, that the MgO starting material (Alfa Aesar 99.998%) had a magnesium deficit of 1.79%. TG measurements with the same material showed a mass loss of 1.43% in two steps during heating to 500 °C. By comparison with equilibrium calculations [4] the two steps could be assigned to the subsequent decomposition of $Mg(OH)_2$ and $MgCO_3$ impurities that lower the Mg assay.

It is difficult to find a commercial iron oxide with precisely defined assay that is suitable to charge iron quantitatively. Under ambient conditions hematite Fe_2O_3 is stable; but depending on T and p_{O_2} wustite FeO (due to oxygen excess more accurately $\approx Fe_{0.947}O$) or magnetite Fe_3O_4 can be formed. The predominance (Ellingham) diagram in Fig. 4 shows 10 fields for stable phases.

The different valencies of iron make it difficult to choose one of the iron oxides as starting material. Iron(II) oxalate $Fe(COO)_2{\cdot}2H_2O$ that is available with 99.999% purity (Alfa Aesar "puratronic") is an alternative choice that allows the more quantitative charging of iron. The thermolysis

$$\mathrm{Fe(COO)_2 \cdot 2H_2O \xrightarrow{argon} FeO + CO_2 \uparrow + CO \uparrow + 2H_2O \uparrow} \tag{4}$$

$$\mathrm{2Fe(COO)_2 \cdot 2H_2O \xrightarrow{air} Fe_2O_3 + 3CO_2 \uparrow + CO \uparrow + 4H_2O \uparrow} \tag{5}$$

leads under reductive or oxidative conditions to a theoretical mass loss of 60.06% (4) or 55.63% (5), respectively. Reductive conditions are maintained, if the decomposition is performed under flowing argon with 99.999% purity (solid line in Fig. 5) and lead to FeO. For $\vartheta \approx 650$ °C the TG signal is almost equal to the theoretical mass loss (4) but slightly ($\approx$0.44%) too large for the product $Fe_{0.947}O$. A continuing small mass loss in the whole "plateau" region $\vartheta = 550$–750 °C indicates, that the composition of the sample is still slightly changing.

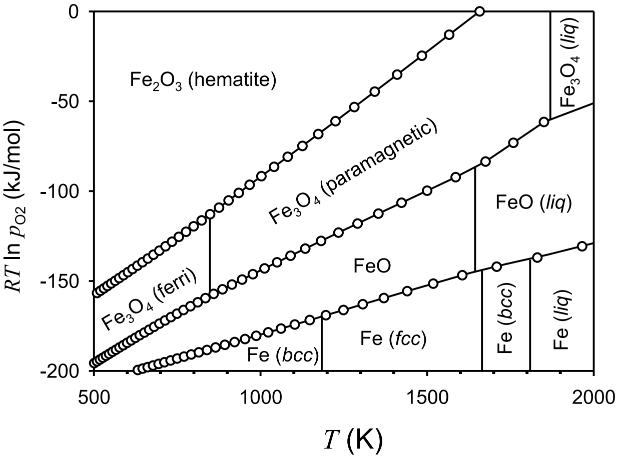

Fig. 4. Ellingliam diagram for the Fe–O system under a total pressure $p = 1$ bar (computed with data from [4,12,13]).

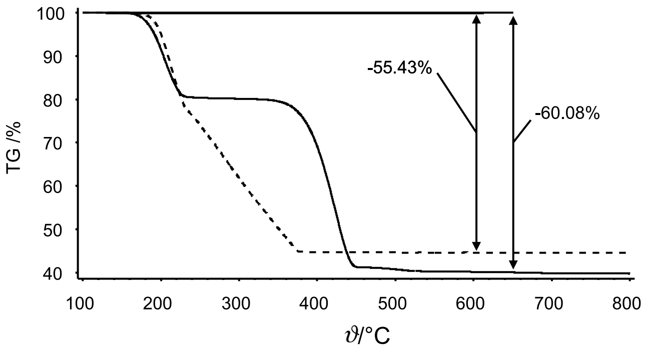

Fig. 5. Full line: TG of 33.89 mg $Fe(COO)_2{\cdot}2H_2O$ (Alfa Aesar puratronic) in argon (40 ml/min). Dashed line: TG of 35.20 mg $Fe(COO)_2{\cdot}2H_2O$ in air.

If the same material is heated in air, the thermolysis leads to Fe_2O_3 (dashed line in Fig. 5). The TG signal does not change further after passing the step at $\vartheta \approx 380$ °C, but the measured TG step $(\Delta m/m)_{\mathrm{exp}} = -55.43\%$ is slightly smaller than the theoretical value -55.63% (5). ICP-OES did not show any significant impurity cation concentrations. The present results did not allow to give an explanation for the remaining differences between theoretical mass loss and measured TG step heights. However, the constant TG signal that is obtained after decomposition in air shows, that pure stoichiometric Fe_2O_3 can be obtained from $Fe(COO)_2{\cdot}2H_2O$ under these conditions. This material is suited for quantitative charging of iron in crystal growth processes.

4. Conclusion

High purity starting materials that are used for the synthesis of oxide materials contain often "unexpected" impurities as hydroxides or carbonates. Such impurities do not disturb the synthesis principally, as they can be removed by a qualified annealing procedure. However, quantitative knowledge on the impurity content is often inevitable to know the assay value of the corresponding starting material and to find experimental conditions that lead to the desired product. Often the combination of ICP-OES and TG measurements proves to be suitable to obtain the desired informations: ICP-OES gives exact quantitative data on the assay value of main components and TG can very often give information on the origin of impurities that alter assay values and on experimental conditions that lead to the desired compounds.

Calcium carbonate $CaCO_3$, magnesium oxide MgO, and lanthanium oxide La_2O_3 are examples for compounds that were found to show usually deviations from the expected assay values. These deviations reach from some tenth of a per cent to as much as >10%. ICP-OES measurements of the other compounds dealt with in this study ($SrCO_3$, $BaCO_3$, Li_2CO_3) resulted in the theoretical assay value and were in agreement with TG curves that showed the expected mass loss during heating. The determination of assay values for metals with different valency (e.g. iron) is more sophisticated than for metals with only one predominant valency. Therefore, the TG step heights that are measured during the decomposition of $Fe(COO)_2 \cdot 2\,H_2O$ differ partially more from the theoretical values than for the alkaline, alkaline earth, or rare earth compounds mentioned above.

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