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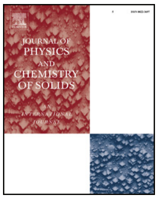

Relative stability of hydrated/anhydrous products of calcium chloride during complete dehydration as examined by high-temperature X-ray powder diffraction

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ABSTRACT

The correlation between the relative stability of hydrated/anhydrous products and microstructure of calcium chloride has been investigated by high-temperature X-ray powder diffraction. The X-ray diffractograms were recorded at 25, 115, 150 and 200 °C, respectively. Results indicate that tetrahydrate and dihydrate are the major forms available at 25 °C. The first endothermic dehydration at around 115 °C is accounted for a mixture of anhydrous calcium chloride and monohydrate. The second consecutive endothermic dehydration at around 150 °C ensured complete removal of crystalline water. The complete dehydration is accounted for two different anhydrous calcium chloride phases with larger (0.324 nm^3) and smaller (0.168 nm^3) unit cell volume. The phase with smaller unit cell volume is the stable anhydrous form of calcium chloride beyond 150 °C. The relative stability of anhydrous/hydrated products at different temperatures simultaneously determines by respective lattice strain, crystallite size, and unit cell volume. It is also found that inferior lattice strain, larger crystallite size, and smaller unit cell volume ultimately account for dominant and more stable calcium chloride product. The moisture absorption from the material takes place towards reducing lattice strain; hence, the hygroscopic nature of calcium chloride can be somewhat related to microstructure stability at low temperatures.

1. Introduction

Despite the hygroscopic nature of the material, numerous investigations have been executed previously on understanding the thermal behavior of calcium chloride. Typically calcium chloride is available in different forms such as anhydrous, hexahydrate, tetrahydrate, dihydrate and monohydrate depending on the number of water molecules incorporated in the crystal lattice. Apparently, the utilization of calcium chloride is substantially increased in recent times due to its imperative application as a primary electrolyte for high-temperature molten salt electrolysis of minerals [1–4] and thermal energy storage material [5–9], etc. Therefore, the thermal behavior and relative stability of calcium chloride products during complete dehydration need to be addressed more specifically to envisage the structural changes and reactivity of the material.

The prevailing literature revealed that the application of X-ray diffraction on structure determination of calcium chloride hydrates in solution at different temperatures was reported by Yamaguchi et al. [10] where the radial distribution function and model fitting were simultaneously employed. Recent developments showed that the thermal behavior of eutectic containing calcium chloride as a thermal energy storage material was greatly investigated by TGA/DTA (Thermo Gravimetric and Differential Thermal analysis) and DSC (Differential Scanning Calorimetry)analysis [5–7]. However, a little or no attention has been received so far to predict the relative stability of hydrated/anhydrous products of calcium chloride during complete dehydration.

The microstructure of materials provides valuable information on structure related modifications and often used for material/process characterization (e.g. characterization of nanomaterials and processes such as phase transformation of quartz) [11–14]. It is quite obvious that vigorous lattice vibrations and sequence of structural rearrangements during dehydration can possibly alter the microstructure of calcium chloride. Therefore, the effect of microstructure on the relative stability of hydrated/anhydrous products of calcium chloride is an imperative topic related to process characterization (dehydration) that has not been addressed in the prevailing literature.

Although the integral breadth (IB) methods are often employed in estimating the microstructure of materials, X-ray line broadening

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analysis plays a significant role in the experimental determination of both lattice strain (ε) and crystallite size (D) [15]. The classical Williamson-Hall uniform deformation model (WH-UDM method) is a well-known approach that entirely addresses the microstructure of a material anchored in the isotropic nature or the uniform lattice strain [11,12,15–20]. Apparently, the classical WH method is still valid when trying to discover the trends in the microstructure of materials undergoing various physical and chemical processes [15].

The investigation of composition and microstructure of hydrated/anhydrous products of calcium chloride is achieved by high-temperature X-ray powder diffraction (XRD). Furthermore, the Thermo Gravimetric Analysis and Differential Thermal Analysis (TGA/DTA) are employed simultaneously in estimating the dehydration temperatures of calcium chloride and weight loss of the material as a function of temperature. Despite the recently updated version of WH method based on size/strain anisotropy and line defects, etc [15,17], the classical WH-UDM is employed in estimating both lattice strain and crystallite size of calcium chloride at elevated temperatures. Since there is no proper literature available on microstructure analysis of calcium chloride related to complete dehydration, the present study made an attempt for the first time to correlate the relative stability of hydrated/anhydrous products with the microstructure of calcium chloride.

2. Materials and methods

Anhydrous calcium chloride (> 99%) was obtained from Avonchem Limited, Oxon, United Kingdom. The anhydrous form was initially employed to understand the hydration of the material at room temperature, complete dehydration, and the correlation between the relative stability of hydrated/anhydrous products and microstructure at elevated temperatures. Thermal analysis of the material (calcium chloride) was initially carried out using SDT Q600 V20.9 Build 20 TGA/DTA analyzer. The investigation of complete dehydration of calcium chloride was achieved by Rigaku Ultima IV X-ray powder diffractometer equipped with high-temperature sample attachment (X-ray tube with a copper target, scintillation counter as the detector and curved graphite crystal monochromator).

The thermal profile and characteristic dehydration temperatures of calcium chloride were primarily obtained by TGA/DTA analyzer (the initial weight of calcium chloride: 9.7720 mg, ramp: 10 °C min^{-1}, temperature range from 25 °C to 1000 °C, purge gas: high purity nitrogen). The dehydration temperatures determined by TGA/DTA were subsequently employed in X-ray powder diffraction to identify the composition and microstructure of calcium chloride during complete dehydration. The X-ray diffraction analysis was achieved by placing an appropriate amount of anhydrous calcium chloride (a sample obtained from a freshly opened bottle) inside the groove of the platinum sample holder of high-temperature attachment. The X-ray diffractograms were then recorded at 25, 115, 150 and 200 °C (as determined by TGA/DTA analysis) subsequent to 10 min temperature stabilization period. Rigaku programmable temperature controller (PTC-30, externally attached) was occupied to maintain the temperature inside the ceramic furnace chamber of high-temperature attachment throughout the entire period of analysis. The proper placement of thermocouple inside the platinum sample holder was ensured a uniform temperature profile across the sample. The X-ray tube conditions were maintained at around 40 kV (tube voltage), 30 mA (tube current) and 1.2 kW (X-ray power), respectively.

A typical scanning range from 5° to 160° (2θ) was initially selected to obtain diffractograms at each temperature. Both scan rate and sampling width were maintained at around 10° per minute (deg min^{-1}) and 0.1°, respectively. The higher scan rate was employed here to minimize the time frame required for a single scan that further minimized the time frame responsible for ongoing composition changes due to progressive absorption of moisture at room temperature and structural rearrangements accompanied by the removal of crystalline water at elevated temperatures (especially at around 115 °C and above). The X-ray diffraction analysis was also carried out under apposite slit combination in such that the divergence slit, scattering slit and receiving slit were maintained at around 2/3°, 2/3° and 0.45 mm, respectively. The composition of calcium chloride at different temperature (25, 115, 150 and 200 °C) was estimated using Relative Intensity Ratio (RIR) of each phase that was accurately assigned by PDXL2 software along with ICDD database (The International Centre for Diffraction Data). The respective unit cell volumes of hydrated/anhydrous products of calcium chloride were also extracted by correctly retrieved phases.

The microstructure analysis was achieved by taking full width at half maximum (FWHM) values of selected reflections of calcium chloride products at different temperatures (between 10° and 50° at 25 °C, 10° - 60° at 115 °C, 10° - 65° at both 150 and 200 °C) by eliminating instrumental peak broadening with respect to NIST silicon standard 640 d. Both crystallite size (D) and lattice strain (ε) of hydrated/anhydrous products of calcium chloride at specified temperatures were graphically estimated by traditional Williamson-Hall uniform deformation model (WH-UDM). Although the crystallite size (size-induced) and lattice strain (strain-induced) independently contributed to total X-ray peak broadening, the full widths at half maximum values (FWHM) were substituted in the classical WH-UDM equation to acquire both parameters. According to the WH-UDM, both strain-induced (β_ε) and size-induced (β_D) peak broadening can be related to total X-ray peak broadening (β_{hkl}) as given below [11,19],

$$\beta_{hkl} = \beta_D + \beta_\varepsilon \tag{1}$$

The size-induced peak broadening depends on both crystallite size (D) and $1/\cos\theta_{hkl}$. In contrast, the lattice strain (ε) and diffraction angle ($\tan\theta_{hkl}$) determine the magnitude of strain-induced peak broadening [12,15]. Therefore, the classical WH-UDM equation can be derived by assuming isotropic nature of crystal (uniform strain in all the crystallographic directions) and independent contribution of both strain-induced and size-induced peak broadening on total X-ray peak broadening as follows [11,12],

$$\beta_{hkl} = \frac{K\lambda}{D\cos\theta_{hkl}} + 4\varepsilon\tan\theta_{hkl} \tag{2}$$

The rearrangement of Eq. (2) considering $\tan\theta_{hkl} = (\sin\theta_{hkl}/\cos\theta_{hkl})$, the classical WH-UDM equation can be obtained as follows,

$$\beta_{hkl}\cos\theta_{hkl} = 4\varepsilon\sin\theta_{hkl} + (K\lambda/\mathbf{D}) \tag{3}$$

Where D, K, ε, and λ are the crystallite size, shape factor (K = 0.90), lattice strain and wavelength of X-rays (λ = 0.154056 nm), respectively. The magnitude of lattice strain and crystallite size were obtained using the respective gradient (slope) and intercept of WH plot between $\beta_{hkl}\cos\theta_{hkl}$ (on the y-axis) and $4\sin\theta_{hkl}$ (on the x-axis).

3. Results and discussion

3.1. Composition variations and effect of unit cell volume on the relative stability

The X-ray diffractograms of calcium chloride recorded at selected temperatures (25, 115, 150 and 200 °C) clearly exemplified the composition of calcium chloride during complete dehydration. Although the starting material was in the form of anhydrous calcium chloride, the hydrated products were readily available at room temperature due to hygroscopic nature of the material. The tetrahydrate ($CaCl_2·4H_2O$, unit cell volume – 0.328 nm^3) and dihydrate ($CaCl_2·2H_2O$, unit cell volume – 0.530 nm^3) are the major forms of hydrated calcium chloride available at around 25 °C (Fig. 1).

The prevailing literature reported that $CaCl_2·3H_2O$ and $CaCl_2·2H_2O$ are the major forms of hydrated calcium chloride available at around