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Preparation of ultrafine CsCl crystallites by combined cryogenic and room temperature ball milling

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Abstract

The present investigation reports the preparation and microstructural characterization of ultrafine CsCl crystallites using combined cryogenic and room temperature (RT) mechanical milling. The milling has been performed in evacuated WC vials under high purity argon atmosphere. The low temperature milling has been utilized as an effective means of rapid fracturing of the CsCl crystallites. This was followed by RT milling for different time durations. The final crystallite size obtained is 10 ± 6 nm for sample cryo-milled for 11 h and subsequently RT milled for 35 h. The experimental findings indicate the strong effect of duration of cryo-milling on the final size of the crystallites. The prolonged room temperature milling leads to increase of the crystallite size due to deformation-induced sintering. The results have been discussed in the light of currently available literature.

Keywords: A. Sintering; CsCl; Cryogenic temperature; Ball milling; Nanocrystallites

1. Introduction

Cesium chloride (CsCl), the family member of alkali halides (AH), is one of the most popular and important materials for mankind from ancient times. A great deal of research work on CsCl has been carried out in various fields of science and engineering due to its useful optical properties, i.e., the presence of colour centres [1,2]. The alkali halides with colour centres are considered to be promising systems for applications in new optical devices such as waveguides and nanolaser (nanometer-sized crystallites for lasing). The nanolasers are deemed to be a key element in realizing an optical computer on a single-semiconductor chip or any integrated optical fibre communication devices [3]. The fabrication of nanolasers requires preparation of nanocrystalline CsCl. The molecular beam epitaxy (MBE) techniques have made it possible to produce various types of nanostructures consisting of CsCl [4]. It has attracted lots of attention because of tremendous potentials for the purpose of miniaturizing electronic devices [5]. Thus, preparation and characterization of nanocrystalline CsCl is utmost important for application of such devices.

The ultrafine CsCl can be prepared by several experimental techniques. This includes both bottom-up and top-down approaches of nanomaterials production [4]. MBE, as mentioned earlier comes under the former category. Alkali halides are very reactive and therefore, chemical synthesis processes cannot be utilized for preparation of ultrafine CsCl. The most common technique utilizing the top-down approach is the mechanical milling. This process is carried out in a high-energy ball mill. It involves repeated deformation, cold-welding, fracturing and dynamic recrystallization to obtain ultrafine nanoparticles [6]. The impact force exerted by the balls on the powder causes plastic deformation leading to strain hardening and ultimately fracture. The main advantage of this process is the reduction of crystallite size to nanometric regime. A large volume of research work has been carried out on the preparation of metallic, oxide, nitride, boride nanocrystallites using ball milling. To the best of the authors' knowledge, a very few research work has been reported in the literature on preparation and characterization of halide nanocrystals [7]. The

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present work reports, for the first time, the preparation and detailed microstructural characterization of CsCl nanocrystallites by combined cryogenic and room temperature ball milling.

Cryo-milling is a kind of mechanical milling in which metallic or ceramic powders are ball milled in liquid-nitrogen (LN_2) slurry or at cryogenic temperatures. It is well known that the cooling of powders is an effective way to accelerate the fracturing process [9–11]. The extremely low temperature in cryo-milling suppresses recovery and recrystallization processes, causing rapid grain refinement [9]. It has been shown by Mohamed et al. [12] that the ultimate grain size obtained in the mechanical milling is determined by balance of following factors: (i) defect generation and (ii) recovery and recombination of defects during plastic deformation. The defect generation and the recovery kinetics are strong function of temperature [11]. It is well know that dynamic recovery can effectively be suppressed by low temperature milling for many materials [10]. On the other hand, at extremely low temperature, the plastic deformation is very limited and therefore, defect generation and recombination are not sufficient to obtain finer grain size. RT milling will lead to generation as well as annihilation of defects such as dislocations. Therefore, it is expected that combined cryo and RT milling will cause refinement of grain size. In the present investigation, such a study is carried out on CsCl, which is brittle at low temperature [2]. The idea of the using combined cryo and RT milling also originates from our previous study on preparation of nanocrystalline KCl crystallites using RT milling under Ar atmosphere [11]. The results of the investigations reveal that the crystallite size cannot be reduced below 90 nm even after 30 h of RT milling of KCl [11]. In fact, longer RT has been found to cause increase of crystallite size due to sintering.

2. Experimental details

Pure CsCl powder (Merck, Germany) was ball milled in a modified P0 (Pulverisette, Fritsch, Germany) mill using four 15-mm-diameter tungsten carbide (WC) balls in WC vial. The ball to powder weight ratio was kept as 20:1 at low temperature (77 K) as well as room temperature (RT). The low temperature in the vial was created by pouring a mixture of liquid nitrogen (LN_2) and methanol in an annular jacket around the vial. The powder in vial was not in contact with LN_2, thereby there was no contamination from coolant. The temperature of the sample was measured by resistance temperature detector (RTD) probe attached to the vial. The vials loaded with powder and ball, were evacuated using a vacuum pump to a pressure of 10^{-2} mbar before backfilling with argon gas. Milling was stopped intermittently to ensure the vacuum in the vial. Cryo-milling times ranged from a few hours to 11 h. The room temperature milling (RT milling) was carried out in the same mill with similar milling parameters. The milling time in RT milling was varied from few hours to 55 h. The samples taken out at different time durations were stored in the vacuum desiccators. Sufficient care had been taken to ensure that no contamination taking place during milling.

The milled powders were examined by X-ray diffraction technique using a Pan analytical Xpert Pro X-ray powder diffractometer with Cu Kα radiation (λ = 0.154056 nm). The peak shift was corrected using Si as an external standard. Before recording the XRD pattern of the milled CsCl powder, Si was sprinkled on the powder sample to precisely record the peak shift of the CsCl peaks due to mechanical milling. Microstructural analysis was performed using Scanning electron microscope, SEM (FEI SIRION XL 40 SFEG) operating at 5 kV and transmission electron microscope, TEM (Technai F30) operating at 100 kV. As radiation damage had been a problem for observation of CsCl in TEM, sufficient care had been taken to minimize radiation damage. The milled CsCl powders were mounted on Cu-grid of high mesh number (600 mesh size) so that charging could be avoided. Working quickly at low intensity (smaller condenser aperture) and at lower accelerating voltage had not been sufficient enough to obtain good quality images with minimum radiation damage. The samples were cooled to liquid nitrogen temperature using a cryo-holder (Gaton, PA, USA) to obtain good quality images.

3. Results

3.1. X-ray diffraction

Fig. 1 depicts the X-ray diffraction patterns of milled CsCl samples for different milling conditions. The positions of all the peaks are marked at the bottom of the figure. The Si peaks are marked by dashed lines. Si is used as an external standard to determine the peak shift due to size reduction and strain in the milled powder. All the other peaks in the diffraction patterns can be indexed using the reflections of CsCl. Therefore, the presence of any contaminants cannot be detected in the milled powder.

3.2. Scanning electron microscopy (SEM)

Now let us discuss the microstructural evolution of CsCl powder during ball milling. We have carried out cryo and RT milling of CsCl powder for different durations to study the effects of milling hours on final crystallite size. The process of mechanical milling of powders normally involves repeated welding, fracturing and rewelding of powder particles. This leads to reduction of crystallite size due to plastic deformation [6,8–10,12]. Fig. 2a is the SEM micrograph of the starting powder showing large particles (50–150 μm) with irregular morphology. As compared to the starting microstructure, several important characteristics can be observed in cryo-milled powders. Fig. 2b shows scanning electron micrograph (SEM) of powder cryo-milled for 7 h with insets showing magnified image. It is clearly observed that the particle size (1–2 μm) has extensively been reduced during cryo-milling as shown in the inset of Fig. 2b revealing small crystallites. One can also observe the presence of the fragmented finer crystallites as indicated by white arrows on the higher magnification micrograph. Fig. 2c is the representative