

Size effect on the lattice parameter of KCl during mechanical milling

Prithu Sharma,^{a,†} Krishanu Biswas,^{b,*} Amit Kumar Mondal^c and Kamanio Chattopadhyay^c

^aDepartment of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai, Tamilnadu, India

^bDepartment of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur, Uttar Pradesh, India

^cDepartment of Materials Engineering, Indian Institute of Science, Bangalore, Karnataka, India

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The size effect on the lattice parameter of ionic KCl nanocrystals was studied systematically during mechanical milling of pure KCl powder under vacuum. The results suggest anomalous lattice expansion, with the lattice parameter increasing from 6.278 Å at $d = 6 \mu\text{m}$ to 6.30307 Å at $d = 85 \text{ nm}$. The defects generated during ball milling of KCl and surface stress are deemed to be responsible for this lattice parameter expansion.

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The properties of nanocrystals are significantly different from their bulk counterparts. Many interesting phenomena are expected to happen when the grain size of any material is reduced to the nanoscale. One such phenomenon of current interest is the change in the lattice parameter of ionic crystals when the crystallite size is so reduced [1–4]. In contrast to the lattice contraction found in metal nanocrystals, most ionic metal oxides exhibit lattice expansion as the particle size is reduced. Nanoparticles of CeO_2 , TiO_2 , BaTiO_3 and SrTiO_3 have been studied extensively to investigate this effect [1–4]. Subsequently, efforts have been made to explain this anomalous behavior in these oxide nanoparticles. Tsunekawa et al. [1,2] proposed that lattice expansion in CeO_2 nanocrystals is due to the reduction in electrostatic force caused by valency reduction from Ce^{4+} to the larger Ce^{3+} . For BaTiO_3 nanocrystals, using ab initio calculations, these authors showed that the increase in ionicity of Ti ions was responsible for the expansion of the lattice [2]. Li et al. [3] proposed a surface-defect induced dipole model to explain anomalous expansion of tetragonal rutile lattice. The surface dipole model was used to explain anomalous lattice expansion in

terms of strong interactions among surface dipoles, which then produce negative pressure. In the case of SrTiO_3 [4], it has also been argued that the lattice expansion is due to enhanced surface-defect dipoles causing a negative pressure effect. Hence, the anomalous lattice expansion studied in oxide ionic nanoparticles has been attributed to the change in valency of the cation or surface dipole formation. Whether such an anomalous lattice expansion in the ionic nanoparticles is a universal phenomenon needs to be investigated. To the best of the authors' knowledge, there has been no investigation of ionic nanoparticles where neither of these effects is possible.

In the present study, we report the anomalous expansion of a lattice of KCl nanoparticles prepared using vacuum ball milling. KCl is highly ionic in nature, and the formation of a dipole or a change in ionicity cannot occur. However, defects such as vacancies (Schottky type) and/or interstitials (Frenkel type) can form during ball milling. The presence of defects in the nanoparticles generated during vacuum ball milling and the surface stress generated can be deemed responsible for the anomalous lattice expansion of KCl.

Pure KCl powder (Merck, Germany) was ball milled in a Fritsch P7 (Fritsch, Germany) mill using six 15 mm diameter stainless steel balls in stainless steel vials. The ball to powder weight ratio was kept at 8:1. The vials, loaded with powder and ball, were evacuated using a

* Corresponding author. Tel.: +91 512 2596184; fax: +91 512 2597505; e-mail: kbiswas@iitk.ac.in

† Now at MIT, Boston, MA, USA.

vacuum pump to a pressure of 10^{-2} mbar before milling. Milling was stopped intermittently to evacuate the vials to ensure that the vacuum level was maintained. Milling times ranged from a few minutes to 30 h. Samples were removed at different times and stored in vacuum desiccators with kerosene to prevent any reaction with moisture. The milled powders were examined using X-ray diffraction technique using a JEOL JDX-8030 X-ray powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm). The peak shift was corrected using Si as an external standard. The change in the lattice parameter was calculated using the least squares method. The uncertainty of the lattice parameter obtained was within ± 0.0005 Å. The crystallite size was measured using transmission electron micrographs. Microstructural analysis was performed using a transmission electron microscope (TEM, Technai F30) operating at 100 kV. As radiation damage has always been a problem for observation of KCl in a TEM, sufficient care had to be taken to minimize radiation damage. Working quickly at low intensity (smaller condenser aperture) and at a low 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 cryoholder (Gaton, PA, USA) to obtain good quality images.

Figure 1 shows the X-ray diffraction patterns of KCl power vacuum milled as a function of milling time. The peaks of both KCl and Si are marked. As already mentioned, Si powder was used as an external standard. The

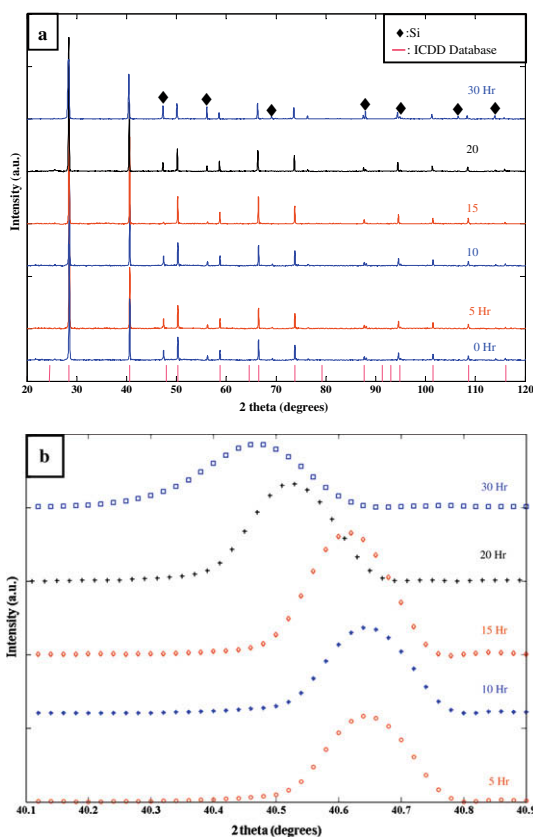


Figure 1. (a) X-ray diffraction patterns of KCl with Si. (b) Enlarged view of the (2 2 0) peak of KCl showing the peak shift and broadening.

vertical lines at the bottom of the figure indicate the positions of the KCl peaks as per the ICDD database. The intensities of some of the KCl peaks (such as (1 1 1), (3 1 1), (3 3 1) and (5 1 1)) were too weak to be observed. The inset of Figure 1 shows a magnified view of the (2 2 0) peak of KCl powder milled for different times. The (2 2 0) peak shows a significant shift to lower angles with longer milling time, indicating lattice expansion. The precise lattice parameter of milled samples for different times was calculated by the least squares method using a set of data from each X-ray diffraction pattern. The patterns also become broad (Fig. 1b) with decreasing crystallite size but maintain the face-centered cubic structure of KCl (space group $Fm\bar{3}m$) as a function of milling.

The diffraction data were analyzed based on the Gaussian distribution [5], which incorporates both crystallite size and lattice strain broadening:

$$(\beta \cos \theta)^2 = (\lambda/d)^2 + (2\eta \sin \theta)^2; \beta = \beta_G - \beta_b \quad (1)$$

where θ is the Bragg angle, λ is the X-ray wavelength, d is the particle diameter, η is the lattice strain, β_G is the integral width of Gaussian distribution and β_b is the instrumental broadening. The peak shapes are indeed Gaussian (Fig. 1b).

The experimental results are presented as the change in lattice parameter ($\Delta a = a - a_0$, where a_0 is bulk lattice parameter) as a function particle size in Figure 2. The lattice parameter of the bulk KCl (a_0) is 6.278 Å [6].

The average crystalline size of all the samples reported here was measured using the TEM. It is evident that the lattice parameter of the milled KCl crystallites indeed increases as the crystallite size decreases. Before discussing the origin of such lattice expansion, we present the results obtained from the representative sample using the TEM. Figure 3a shows a TEM bright-field image of the starting powder. The particles are very large (~ 5 – 6 μm) and have a cuboidal shape. The representative low magnification bright-field electron micrographs of sample milled for 20 and 30 h are shown in Figures 3b and 3c and reveal the particle size and morphology. It is evident that the particle size decreases as the milling time increases. The morphologies of the particles are shown as insets in the figures. The inset of Figure 3b shows that the crystallites have a spherical shape. This micrograph was obtained when the particle was oriented along the [0 0 1] direction. In the case of the sample milled for

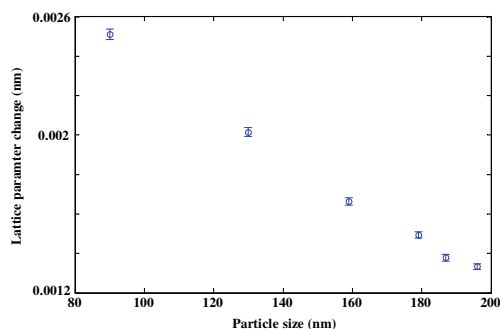


Figure 2. Plot showing the change in lattice parameter of KCl nanoparticles as a function of size of the particle.

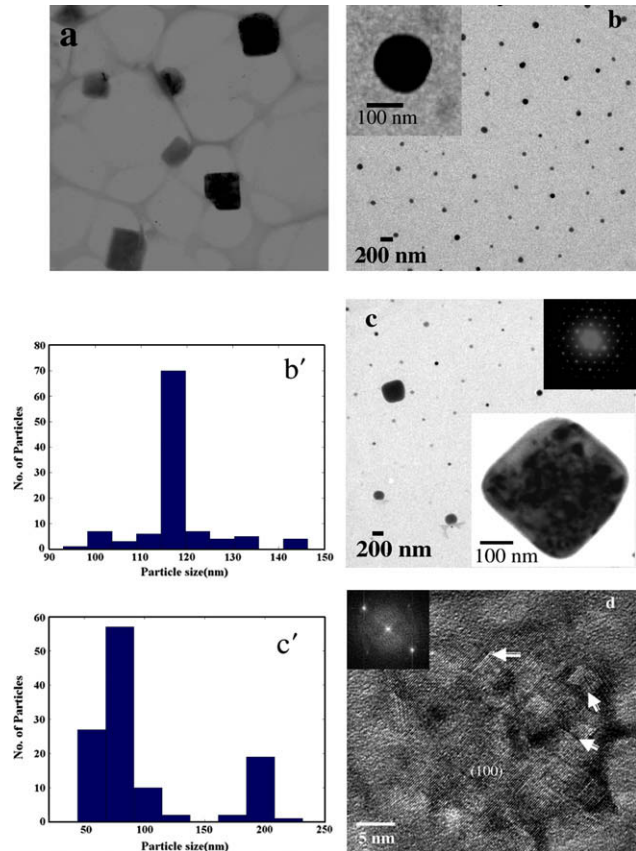


Figure 3. Bright-field TEM images of samples milled for (a) 0 h; (b) 20 h; (c) 30 h. The insets in (b) and (c) show higher-magnification images of the KCl crystallites. (b' and c') Particle size distributions of the 20 and 30 h milled samples; (d) high-resolution image of one KCl nanocrystal showing the presence of defects; the inset shows the FFT along the [0 0 1] direction. The top insets of (a) and (b) each show a higher-magnification image of one crystallite. The bottom inset of (b) shows a SAD pattern from one of the bigger KCl particles along the [0 1 1] direction, with the inset showing a blown up view of the SAD pattern.

30 h we observed a bimodal particle size distribution, with some of the particles having a much larger size than the majority. The bigger particles have a cuboidal morphology, whereas the smaller majority of the particles are spherical. The selected area diffraction (SAD) pattern from one of the spherical particles is shown as the upper inset of Figure 3b. The average particle size of each sample was determined following statistical distribution of the size of the particles using the transmission electron micrographs for each sample. Sufficiently large numbers of particles were analyzed to obtain a statistical distribution. The mean value of the distribution is reported. Figure 3b' and c' shows such analysis for the 20 and 30 h milled samples. Figure 3b' indicates a monosized distribution whereas Figure 3c' shows a bimodal distribution. The detailed microstructural analysis is under study and will be communicated separately [7]. Thus, the plot shown in Figure 2a indicates a definite trend suggesting that the KCl lattice parameter increases as the crystallite size decreases. This result is unique as well as new in the sense that the lattice expansion is due to reduction of particle size of ionic nanoparticles.

Let us now discuss the origin of the lattice expansion of KCl nanocrystals prepared by vacuum ball milling. Several mechanisms have been found to be responsible for the lattice expansion of ionic oxide nanoparticles, as mentioned earlier [1–4]. However, these mechanisms cannot be applied to KCl nanocrystals because neither a change in ionicity nor surface dipole formation is possible in the KCl molecule. Recently, the Madelung model was developed to predict the lattice parameter expansion of CeO_2 and BaTiO_3 nanocrystals [8]. According to this model, the optimal lattice parameter (a_0) is decided by the balance between the long-range Coulomb attractive force and short-range repulsive interactions [8], and this balance is altered by the presence of the surfaces of nano-sized particles. This model was used to explain the lattice parameter expansion of CeO_2 and BaTiO_3 particles having a size of 4–20 nm [8]. However, this model cannot be applied in the present investigation because the particle size of the KCl obtained during ball milling is in the range of 85–200 nm.

The anomalous lattice expansion KCl nanoparticles can be attributed to the formation of defects in the ionic solid and surface stress [9]. Figure 3c shows a high-resolution image of a KCl crystallite after 30 h of milling, with the inset showing a fast Fourier transform (FFT) of the image. The image reveals the presence of a large number of defects (marked by white arrows) on the surface of a nano-sized KCl crystallite. Conventional electron microscopic observations reveal the presence of dislocations in the milled particles (not shown here).

It is reasonable here to consider that the lattice expansion was caused by induced atomic displacement leading to point defects during ball milling. It has been reported in the literature [9,10] that the displacement of atoms leads to the formation of either Frenkel- or Schottky-type defects in KCl crystallites. A Frenkel defect forms when an ion leaves its place in the lattice and becomes an interstitial by lodging in a nearby location, leaving behind a vacant site. An equal number of vacancies and interstitials is created because of this atomic displacement. On the other hand, a Schottky defect is produced when a pair of ions at normal lattice sites comes to the surface, leaving vacancies behind. It has been reported in the literature [11] that the fractional expansion of the lattice parameter due to point defect concentration c_i can be expressed as

$$\frac{\Delta a}{a_0} = \left(\frac{c_i}{3}\right) \left(\frac{V_{\text{rel}}^i + V_{\text{rel}}^v}{\Omega}\right) \quad (2)$$

where V is the atomic volume and V_{rel}^i and V_{rel}^v are relaxation volumes around an interstitial and a vacancy, respectively. Ω is the molar volume. According to Corish and Jacobs [12], the free volume of formation of vacancy in a Schottky defect, $\frac{V_{\text{rel}}^v}{\Omega}$, is positive for KCl crystals and has a value of $\frac{V_{\text{rel}}^v}{\Omega} = 0.5$. The reported value of the relaxation volume of the Frenkel pair in KCl is about one-quarter of a molar volume [13]. Therefore, the lattice parameter expansion could be explained by a reasonable concentration of interstitials or vacancies. By using $V_{\text{rel}}^i + V_{\text{rel}}^v = 0.75 \Omega$, the point defect concentration is of the order of 10^{20} cm^{-3} in power ball milled for 30 h. The separation of vacancy and interstitial concen-

trations is not possible with the present calculation. This calculation clearly indicates a high concentration of point defects in ball-milled KCl nanocrystals.

Another possible effect that could explain the lattice expansion in KCl nanocrystals is the surface stress [14]. The surface stress f is defined as the reversible work done per unit area due to elastic deformation and is given by

$$f = \gamma + A \frac{d\gamma}{dA} \quad (3)$$

where γ is the surface energy and A is the area of the particle. It is evident from Eq. (3) that the value of f can be either positive or negative because the term $\frac{d\gamma}{dA}$ can be positive or negative for different groups of materials. The theoretical calculations and experimental measurements indicate that both positive and negative stresses are possible in practical systems depending upon the surface structure [15]. The results obtained in the present investigation are consistent with a negative surface stress. The surface stress in a particle of radius r is given by [14,16,17]

$$f = -1.5rK\varepsilon = -0.75DK \frac{\Delta a}{a} \quad (4)$$

where ε is the linear strain, K is the bulk modulus and D is the diameter of the particle. For a KCl particle of diameter 85 nm, the surface stress would be -4.45 N m^{-1} , with $K = 17.36 \text{ GPa}$ [18]. No reliable experimental measurement of surface stress of KCl crystals is available in the literature. The surface stresses of bulk KCl have been theoretically calculated by a number of authors [19–22]. Estimates by Shuttleworth [19] indicate negative surface stress for the $\{1\ 0\ 0\}$ and the $\{1\ 1\ 0\}$ faces of KCl crystals. Benson and Yun [20], Nicholson [21] and Tasker [22] showed that the surface stress of relaxed $\{1\ 0\ 0\}$ and $\{1\ 1\ 0\}$ faces are positive. However, for unrelaxed surfaces, these authors indicated that the surface stresses will have negative values. Tasker [22] clearly demonstrates that, for $\{1\ 1\ 0\}$ relaxed surfaces of KCl, the term $\frac{d\gamma}{dA}$ becomes negative and thus the surface stress for $\{1\ 1\ 0\}$ surfaces for nano-sized particles can have negative values. The bright-field images of KCl particles for 20–30 h show that the particles have undergone a deformation-induced shape change, from a cuboidal shape in the unmilled sample to a near-spherical shape. Because the surface structure of these fine particles is altered, it is expected that the surface stress will also be altered. Theoretical calculations [19] suggest that the surface stresses for the $\{1\ 0\ 0\}$ and $\{1\ 1\ 0\}$ surfaces of bulk KCl are -0.4 and -0.52 N m^{-1} , which is one order of magnitude lower than the calculated value in the present case. However, for nanocrystals, the value of the surface stress will be modified by the increased surface area and deformation. It should be mentioned that the surface is deemed partly responsible for the lattice

expansion. Therefore, the amount of surface stress required to explain the lattice expansion will be less than -4.45 N m^{-1} .

The lattice parameter expansion of vacuum-milled KCl crystallites may thus be explained by the combined effect of defect formation and negative surface stress.

In summary, the influence of the crystallite size of ionic KCl on the lattice was investigated. Lattice expansion indeed takes place during ball milling of KCl powder. An attempt was made to relate this anomalous lattice expansion in KCl nanoparticles to the defects and surface stress developed during ball milling. The microstructural investigation reveals the formation of defects in KCl nanoparticles during ball milling.

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- [1] S. Tsunekawa, R. Sivamohan, S. Ito, A. Kasuya, T. Fukuda, *Nanostruct. Mater.* 11 (1999) 141.
- [2] S. Tsunekawa, K. Ishikawa, Z.-Q. Li, Y. Kawazoe, A. Kasuya, *Phys. Rev. Lett.* 85 (2000) 3440.
- [3] G. Li, J.B. Goates, B.F. Woodfield, *Appl. Phys. Lett.* 85 (2004) 2059.
- [4] X.W. Wu, X.J. Liu, *J. Luminescence* 122–123 (2007) 869.
- [5] B.E. Warren, *X-ray Diffraction*, Addison-Wesley, Boston, MA, 1969.
- [6] N. Masciocchi, G. Artioli, *Powder Diffraction* 11 (3) (1996) 253.
- [7] K. Biswas, P. Sharma, A.K. Mondal, K. Chattopadhyay, submitted for publication.
- [8] V. Perebeinos, S.-W. Chan, F. Zhang, *Solid State Commun.* 123 (2002) 295.
- [9] D. Binder, W.J. Sturm, *Phys. Rev.* 96 (6) (1954) 1519.
- [10] H. Piesl, R. Balzer, W. Waidelich, *Phys. Rev. Lett.* 17 (22) (1966) 1129.
- [11] A. Gaber, H. Zillgen, P. Ehrhart, P. Partyaka, R.S. Averback, *J. Appl. Phys.* 82 (11) (1997) 5348.
- [12] J. Corish, P.W.M. Jacobs, *Chemical Society Specialist Periodical Reports*, vol. 2, Surface and Defects Properties of Solids, The Chemical Society, London, 1973.
- [13] M.J. Gillan, *Philos. Mag.* 43 (2) (1981) 301.
- [14] D. Shreiber, W.A. Jasser, *Surf. Sci.* 600 (2006) 4584.
- [15] F. Spaepen, *Acta Mater.* 48 (1) (2000) 31.
- [16] Q. Jiang, L.H. Liang, D.S. Zhao, *J. Phys. Chem. B* 105 (2001) 627.
- [17] J. Weissmüller, *J. Phys. Chem. B* 106 (2002) 889.
- [18] J.D. Levine, P. Mark, *Phys. Rev.* 144 (1966) 751.
- [19] R. Shuttleworth, *Proc. Phys. Soc. A* 62 (1950) 167.
- [20] G.C. Benson, K.S. Yun, *J. Chem. Phys.* 42 (1965) 3085.
- [21] M.M. Nicholson, *Proc. R. Soc. A* 228 (1955) 490.
- [22] P.W. Tasker, *Philos. Mag.* 39 (2) (1979) 119.