

Crystal Mechanics

Sonofragmentation of Ionic Crystals

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Abstract: Mechanochemistry deals with the interface between the chemical and the mechanical worlds and explores the physical and chemical changes in materials caused by an input of mechanical energy. As such, the chemical and physical effects of ultrasound, i.e., sonochemistry, are forms of mechanochemistry. In this paper, the fragmentation of ionic crystals during ultrasonic irradiation of slurries has been quantitatively investigated: the rate of fragmentation depends strongly on the strength of the materials (as measured by Vickers hardness or by Young's modulus). This is a mechanochemical extension of the Bell–Evans–Polanyi Principle or Hammond's Postulate: activation energies for solid fracture correlate with binding energies of solids. Sonofragmentation is unaffected by slurry loading or liquid vapor pressure, but is suppressed by increasing liquid viscosity. The mechanism of the particle breakage is consistent with a direct interaction between the shockwaves created by the ultrasound (through acoustic cavitation) and the solid particles in the slurry. Fragmentation is proposed to occur from defects in the solids induced by compression–expansion, bending, or torsional distortions of the crystals.

Mechanochemical effects change solid particles physically and chemically under mechanical action.^[1] This includes both chemical effects when surfaces of materials are rubbed or when solids are broken.^[2] There are many ways of inducing mechanochemistry in materials, including trituration, grinding, milling and ultrasound.^[3] When mechanical actions are applied to solids, fracture can occur, but our fundamental understanding of the nature of the breakage of solids as a function of their chemical and mechanical properties remains limited. The fragmentation of powders in liquid slurries especially has received relatively little attention.^[4] In this paper, we examine fundamental experiments on the fragmentation of ionic crystals during sonication of slurries and gained new insights on the mechanism of such sonofragmentation.

When a liquid is irradiated with high intensity ultrasound, acoustic cavitation occurs: i.e., bubbles form, oscillate, grow,

and, under certain conditions, implodingly collapse; this collapse can generate intense local heating, with hot spots created transiently with temperatures of < 5000 K, pressures of Kbar, and shockwaves launched into the liquid.^[5] If a bubble collapses near an extended solid surface (i.e., several times the size of the bubble), the collapse becomes asymmetric and a fast-moving stream of liquid (i.e., microjet) impinges on the solid surface.^[6] In contrast, microjets do not form in slurries with fine powders (e.g., particles less than the bubble diameter), but cavitation still occurs, and shockwaves are formed.

The effect of ultrasound on liquid–solid systems depends on the type of materials sonicated. For example, when slurries of malleable powders (e.g., softer metals) were irradiated with ultrasound, interparticle collisions caused surface deformation, agglomeration, and a change in the chemical composition of the particle surface.^[7] In contrast, sonication of slurries of brittle materials (specifically, molecular crystals) caused fragmentation of the crystals through direct interactions between crystals and shockwaves (without decomposition of the individual molecules in the crystals),^[8] which is a major component of sonocrystallization of active pharmaceutical ingredients (APIs).^[9] Whereas previous studies have examined the effects of control variables (e.g., acoustic power density, frequency, liquid, etc.) on particle fragmentation,^[10] there is only one report that examines the influence of the material properties of solids on their fragmentation under ultrasonic irradiation, and that is limited to polymeric solids.^[11]

For ionic and molecular crystals (particularly for APIs), there are a few articles that examine the relationship between the mechanical properties of the particles and their breakage under dry milling or particle impactation.^[12] Hardness and elasticity are two of the most relevant material properties related to fragmentation. There are several ways to measure the hardness of a material, but the Vickers test is the most common.^[13] The Vickers hardness (H_v) of a material is defined by the degree of deformation of the surface by a diamond indenter at a given applied force. The Vickers hardness of alkali halides has been measured systematically.^[14] The elasticity of materials is quantified by Young's modulus (E): stress (force per unit area) versus strain (proportional deformation). For the alkali halides, Young's modulus has also been measured.^[15]

In this study, six different alkali halides with different Vickers hardness and Young's modulus values, were used to investigate the sonofragmentation patterns of ionic crystals. Various parameters, including the crystal size and control variables, were studied to determine their effect on the fragmentation of alkali halide particles. In addition, the mechanism of sonofragmentation of ionic crystals was examined.

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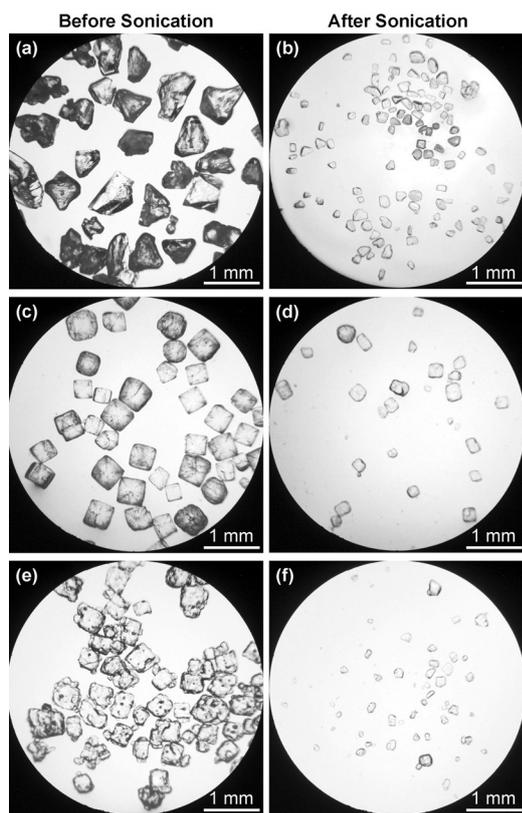


Figure 1. Representative optical micrographs of alkali halide crystals before and after sonication. (a) NaF before sonication and (b) after sonication for 900 seconds; (c) NaCl before sonication and (d) after sonication for 300 seconds; (e) KBr before sonication and (f) after sonication for 90 seconds. Slurries containing 0.2 wt% of the alkali halides in dodecane were sonicated using a titanium horn (10 W cm^{-2} and 20 kHz).

Powders of each alkali halide with relatively narrow size distributions (Figure 1 and Supporting Information Figure S1) were slurried in dodecane at various loading (0.07 to 10 wt.%), and the mixtures were sonicated for various times using a titanium ultrasonic horn (20 kHz, 10 W cm^{-2} ; Sonics and Materials VCX-750). At 20 kHz, the maximum diameter of a cavitating bubble before collapse is $\approx 150 \mu\text{m}$.^[16] All sonication experiments were performed using a 2-second-on and 8-second-off pulse cycle to prevent significant increases in temperature. In all cases, the steady state temperature during sonication was 25°C . Sonication times are reported as the total time that the mixture was exposed to ultrasound. An aliquot of the sonicated slurry was size analyzed by optical microscopy using ImageJ software (National Institutes of Health, Bethesda, MD); approximately 200 particles were measured for each size analysis; in these studies, the size of each crystal was defined as its longest dimension.

Alkali halides were fragmented under ultrasonic irradiation (Figure 1 and Supporting Information Figure S1) and their rates of fragmentation shown in Figure 2. The particle size decreases exponentially with length of time of sonication.

The strength of ionic bonding in alkali halide crystals increases, of course, for smaller cations and anions, e.g., NaF is harder than KBr. Among the alkali halides, increased Vickers

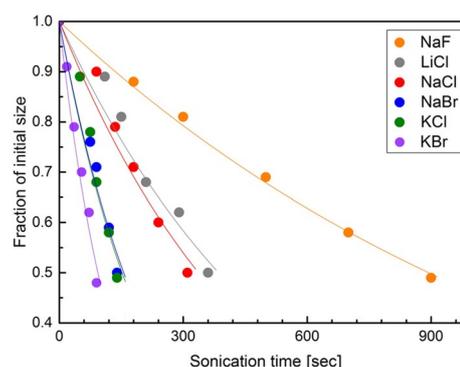


Figure 2. Fraction of initial crystal size versus sonication time for various alkali halides. Slurries containing 0.2 wt% of the alkali halides in dodecane were sonicated using a titanium horn (10 W cm^{-2} and 20 kHz). Solid lines are exponential fits to the data.

hardness and Young's modulus values requires longer sonication times to reach half the initial crystal size (Table 1). When the sonication time is normalized by Vickers hardness or Young's modulus, all values for fraction of initial size are distributed near a master line (Supporting Information Figure S2). That is, the rate of fragmentation monotonically decreases with increasing Vickers hardness or Young's modulus. The quantitative relationship between hardness or elasticity and rate of fragmentation is clear (Figure 3 and Supporting Information Figure S2), but its origins are complicated especially by the critical factor of defect concentration, which does affect the mechanical strength and other properties of materials.^[17]

Table 1. Vickers hardness (H_v), Young's modulus (E), and sonication time necessary to halve the initial crystal size ($\tau_{1/2}$) of alkali halides.^[a]

Alkali halide	H_v (GPa)	E (GPa)	$\tau_{1/2}$ (s)	Initial crystal size (μm)
NaF	0.626	77.5	900	500
LiCl	0.243	49.8	360	580
NaCl	0.216	37.3	310	340
NaBr	0.129	29.7	140	490
KCl	0.128	26.5	140	420
KBr	0.098	22.3	90	310

[a] Determinations of H_v ^[14a,d], E ^[15] and $\tau_{1/2}$ were made on single crystals of the alkali halides. RSD of the initial crystal sizes were around 14%.

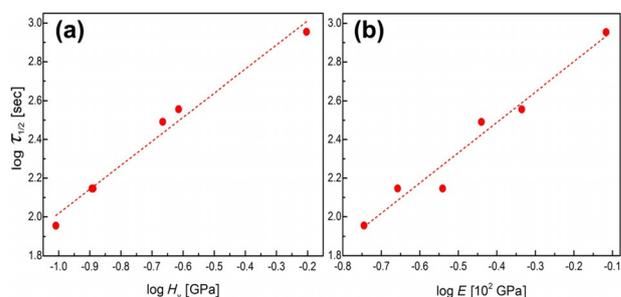


Figure 3. Relationship between (a) Vickers hardness (H_v) and the time necessary to halve the initial crystal size ($\tau_{1/2}$) and (b) Young's modulus (E) and the time necessary to halve the initial crystal size ($\tau_{1/2}$). The dashed lines are linear fits.

For these studies, it was important to establish any consequences of variation in the initial crystal size on sonofragmentation. Sodium bromide was chosen as a test sample and examined at initial crystal sizes ranging from 510 μm down to 150 μm (Supporting Information Figure S3), isolated by sieving using a sonic sifter (Advantech Manufacturing, Berlin, WI). As shown in Figure S4 (Supporting Information), initial crystal size had no effect on the rates of fragmentation of alkali halides over the range examined.

We also studied various control variables to determine their effect on the rate of fragmentation, specifically liquid vapor pressure, viscosity, and slurry loading. Vapor pressure of the slurry was one of control variables examined in this study. When a bubble collapses, the mechanical energy of the expanded bubble before collapse is converted into thermal and chemical energy of the bubble contents, that is, the sonochemical hotspot.^[5c,18] High vapor pressure of polyatomic molecules inside the bubble dramatically decreases the effective temperatures formed in the hot spot both through endothermic bond dissociation of the polyatomic vapor and through the decrease in the polytropic ratio (i.e., the distribution of energy into molecular rotations, bond vibrations, and translations).^[19] Thus, different solvent vapor pressures might cause different rates of particle fragmentation. To test this hypothesis, several organic liquids were used to prepare various potassium chloride slurries. There was no change in the fraction of initial crystal size (Supporting Information Figure S5) as liquid vapor pressure increased from about 0.01 to 50 torr. Thus, the vapor pressure of the slurry did not affect fragmentation of alkali halides crystals. Whereas vapor pressure dramatically affects the temperature reached inside bubbles during cavitation collapse,^[19–20] vapor pressure does not affect either the total mechanical energy of the bubble before the collapse or the bubble rebound that generates the shockwave launched into the liquid.^[7f,9b,21]

Viscosity may also affect the rate of fragmentation by changing relevant factors, such as the number of cavitating bubbles, bubble dynamics, drag on moving particles, and shockwave propagation.^[5a,22] Dodecane and Dow Corning 200 Fluid (i.e., silicone oil) are miscible and were combined to prepare solutions of various viscosities (Supporting Information Figure S6). Slurries of the mixed liquids and potassium chloride were sonicated, and the effect of viscosity on fragmentation was investigated. As the viscosity increased, the rate of potassium chloride fragmentation decreased, as expected (Figure 4). Indeed, for liquid viscosity greater than 100 cSt, no sonofragmentation was observed.

There are four possible contributors to sonofragmentation of materials: interparticle collisions, particle–wall collisions, particle–horn collisions, and particle–shockwave/microjet interactions.^[8] Previous papers on sonocrystallization have often assumed that interparticle collisions play a major role in fragmentation of growing crystals.^[10c,23] Whereas interparticle collisions are important for long ultrasonic irradiation of slurries of metal powders, we found recently that this is not the case for molecular solids.^[8] To understand the breakage of brittle materials, we isolated each of these possible contributors to the

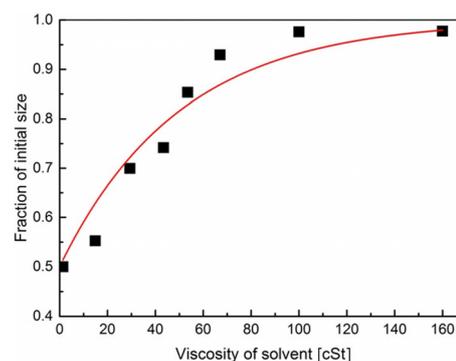


Figure 4. Effect of viscosity on fragmentation of potassium chloride. A slurry containing 0.2 wt% potassium chloride in a dodecane-silicon oil mixture was sonicated using a titanium horn (10 W cm^{-2} and 20 kHz). The solid line is an exponential fit.

sonofragmentation of ionic crystals and examined them separately (Figure 5).

First, we examined the effect of crystal loading on sonicated slurries. Various amounts of potassium chloride were loaded as a slurry into dodecane (10 mL). Regardless of the loading of the slurry, the rate of crystal fragmentation was not significantly affected: 140 seconds of sonication (10 W cm^{-2} , 20 kHz) reduced the initial crystal size to 0.50(3) for slurries ranging from 0.07 to 10 wt% (Supporting Information Figure S7). Thus, interparticle collisions do not contribute significantly to the sonofragmentation of these crystals.

Second, particle–wall decoupling experiments were performed at various ultrasonic intensities. A latex membrane was placed around the potassium chloride slurry to prevent particles from hitting the glass reactor wall (Figure 5b). Although particle–wall collisions did not occur for particles isolated from the wall, these particles showed slightly greater fragmentation than the particles exposed to the wall (Supporting Information Figure S8). The slight increase probably represents the effective increase in ultrasonic intensity that the confined slurry would

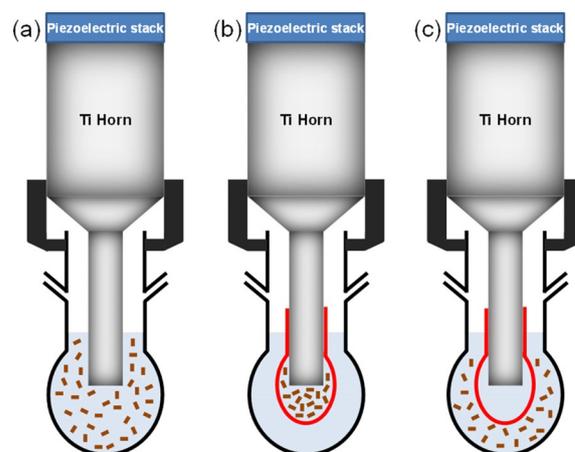


Figure 5. Experimental setups of (a) the normal apparatus showing the immersion of the titanium ultrasonic horn into the slurry, (b) decoupling experiments to eliminate particle–wall interactions, and (c) decoupling experiments to eliminate particle–horn interactions.

have experienced within the membrane. These results demonstrate that particle–wall collisions were not a major mechanism of ionic crystal fragmentation.

Third, particle–horn decoupling experiments were carried out by isolating the potassium chloride slurry from direct contact with the horn using a latex membrane (Figure 5c). The solid particles were still fragmented at rapid rates (Supporting Information Figure S9), even in the absence of direct horn–particle contact. As such, these results demonstrate that particles–horn collisions were also not a major contributor to crystal fragmentation.

Thus, as discussed elsewhere in detail for molecular crystals,^[8] we must conclude that particle breakage of ionic solids irradiated with ultrasound is primarily due to interaction of the solid particles with shockwaves and microjets formed during cavitation, not interparticle collisions or particle impact on hard surfaces (e.g., wall or horn).

For comparison, the mechanisms of crack formation in crystals under mechanical impact from grinding has been previously discussed.^[24] When a solid particle is subjected to a strong impact, tensile stresses are formed radially outward from the initial point of contact. Cracks are generated along these radial lines, leading to eventual particle breakage. In addition, cracks can also be generated perpendicular to the radial cracking, due to the buckling of the particles.

As such, we suggest that there are two general classes of mechanisms for sonofragmentation of ionic (or molecular) crystals: shock-induced compression–expansion and shock-induced bending or torsion, as shown schematically in Figure 6. It is likely that the morphology of the initial crystals will determine the relative importance of these two mechanisms: high aspect ratio solids (i.e., rods, needles, or plates) are much more likely to break through bending and torsion than low aspect ratio solids (as used in these studies).

Breakage of crystals ultimately is a nucleated process due to defects in solids, and is not inherently related to the solids' hardness or bulk modulus. One intuitively expects, however, that the rate at which defects are generated in solid particles during strain or impact ought to correlate with the strength of

materials. This is, if one may, the mechanochemical extension of the Bell–Evans–Polanyi Principle or of Hammond's Postulate: activation energies correlate with enthalpies.^[25] (i.e., activation energies correlate with enthalpies); activation energies for solid fracture correlate with binding energies of solids.

Indeed, prior reports have established empirically that fracture toughness and fracture strength of glasses (both silica and metallic) are empirically proportional to Young's modulus.^[26] There are also similar results for various minerals, and harder minerals required more energy to be broken.^[27] These studies, however, did not examine the kinetics of particle breakage. As we have now observed for ionic solids (Figure 3 and Supporting Information Figure S2), the rate of breakage of ionic crystals correlates strongly with both Young's modulus and the Vickers hardness of these solids: that is, the kinetics of crystal breakage correlates with thermodynamic properties.

In conclusion, fragmentation of various alkali halide crystals was induced by ultrasonic irradiation of slurries in organic liquids; exponential decreases in particle size were observed with length of sonication. Analysis of the fragmentation mechanism showed that direct interaction between alkali halide crystals and shockwaves or microjets, and not interparticle collisions or impaction, were the main cause of sonofragmentation. Shockwave fragmentation of crystals may be induced by either compression–expansion or by bending–torsional effects on the solid particles. There is a strong correlation of the rate of fragmentation with materials' thermodynamic properties (i.e., Vickers hardness and Young's modulus).

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Keywords: crystal engineering · mechanical properties · mechanochemistry · solid-state reactions · sonofragmentation

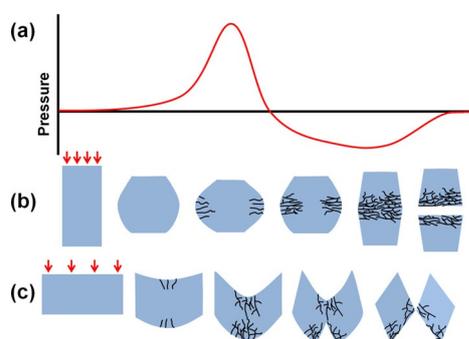


Figure 6. Two classes of mechanisms of shock fragmentation of crystals. (a) Pressure profile of a typical shockwave passing through a liquid; compression and expansion from shockwaves, in general, are not symmetric. (b) Particle breakage from defects formed by shock-induced compression and expansion of the initial crystal and (c) particle breakage from defects created during shock-induced bending or torsion of the initial crystal.

- [1] a) M. K. Beyer, H. Clausen-Schaumann, *Chem. Rev.* **2005**, *105*, 2921–2948; b) W. Jones, M. D. Eddleston, *Faraday Discuss.* **2014**, *170*, 9–34; c) M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755–5798; d) T. Friščić, S. L. James, E. V. Boldyreva, C. Bolm, W. Jones, J. Mack, J. W. Steed, K. S. Suslick, *Chem. Commun.* **2015**, *51*, 6248–6256.
- [2] a) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friscic, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413–447; b) K. Ralphs, C. Hardacre, S. L. James, *Chem. Soc. Rev.* **2013**, *42*, 7701–7718; c) B. Lee, Z. Niu, J. Wang, C. Slebodnick, S. L. Craig, *J. Am. Chem. Soc.* **2015**, *137*, 10826–10832.
- [3] a) G. Cravotto, E. C. Gaudino, P. Cintas, *Chem. Soc. Rev.* **2013**, *42*, 7521–7534; b) K. S. Suslick, *Faraday Discuss.* **2014**, *170*, 411–422; c) P. Cintas, G. Cravotto, A. Barge, K. Martina, in *Polymer Mechanochemistry*, Vol. 369, Springer International Publishing, Switzerland **2015**.
- [4] a) Z. Guo, A. G. Jones, N. Li, S. Germana, *Powder Technol.* **2007**, *171*, 146–153; b) R. M. Wagterveld, L. Boels, M. J. Mayer, G. J. Witkamp, *Ultrasound. Sonochem.* **2011**, *18*, 216–225.
- [5] a) T. Leighton, *The Acoustic Bubble*, Academic press: Cambridge, **2012**; b) K. S. Suslick, *Science* **1990**, *247*, 1439–1445; c) K. S. Suslick, D. J. Flannigan, *Annu. Rev. Phys. Chem.* **2008**, *59*, 659–683; d) R. Pecha, B. Gompf, *Phys. Rev. Lett.* **2000**, *84*, 1328–1330.

- [6] a) J. R. Blake, G. S. Keen, R. P. Tong, M. Wilson, *Philos. Trans. R. Soc. London Ser. A* **1999**, *357*, 251–267; b) W. Lauterborn, A. Vogel, *Annu. Rev. Fluid Mech.* **1984**, *16*, 223–244; c) D. G. Shchukin, E. Skorb, V. Belova, H. Mohwald, *Adv. Mater.* **2011**, *23*, 1922–1934.
- [7] a) T. Prozorov, R. Prozorov, K. S. Suslick, *J. Am. Chem. Soc.* **2004**, *126*, 13890–13891; b) K. S. Suslick, S. J. Doktycz, *J. Am. Chem. Soc.* **1989**, *111*, 2342–2344; c) K. S. Suslick, D. J. Casadonte, S. J. Doktycz, *Solid State Ionics* **1989**, *32–33*, 444–452; d) K. S. Suslick, D. J. Casadonte, S. J. Doktycz, *Chem. Mater.* **1989**, *1*, 6–8; e) D. Radziuk, D. Grigoriev, W. Zhang, D. Su, H. Moehwald, D. Shchukin, *J. Phys. Chem. C* **2010**, *114*, 1835–1843; f) S. J. Doktycz, K. S. Suslick, *Science* **1990**, *247*, 1067–1069.
- [8] B. W. Zeiger, K. S. Suslick, *J. Am. Chem. Soc.* **2011**, *133*, 14530–14533.
- [9] a) N. S. Deora, N. N. Misra, A. Deswal, H. N. Mishra, P. J. Cullen, B. K. Tiwari, *Food Engineering Reviews* **2013**, *5*, 36–44; b) J. R. G. Sander, B. W. Zeiger, K. S. Suslick, *Ultrason. Sonochem.* **2014**, *21*, 1908–1915; c) Z. Zhang, D.-W. Sun, Z. Zhu, L. Cheng, *Compr. Rev. Food Sci. Food Saf.* **2015**, *14*, 303–316.
- [10] a) K. R. Gopi, R. Nagarajan, *IEEE Trans. Nanotechnol.* **2008**, *7*, 532–537; b) L. Zhang, V. Belova, H. Wang, W. Dong, H. Moehwald, *Chem. Mater.* **2014**, *26*, 2244–2248; c) V. Raman, A. Abbas, *Ultrason. Sonochem.* **2008**, *15*, 55–64; d) B. Ambedkar, R. Nagarajan, S. Jayanti, *Ind. Eng. Chem. Res.* **2011**, *50*, 13210–13219; e) F. Franco, L. A. Perez-Maqueda, J. L. Perez-Rodriguez, *J. Colloid Interface Sci.* **2004**, *274*, 107–117.
- [11] G. J. Price, A. J. White, A. A. Clifton, *Polymer* **1995**, *36*, 4919–4925.
- [12] a) M. Meier, E. John, D. Wieckhusen, W. Wirth, W. Peukert, *Powder Technol.* **2009**, *188*, 301–313; b) L. Vogel, W. Peukert, *Powder Technol.* **2003**, *129*, 101–110; c) L. J. Taylor, D. G. Papadopoulos, P. J. Dunn, A. C. Bentham, N. J. Dawson, J. C. Mitchell, M. J. Snowden, *Organic Process Research & Development* **2004**, *8*, 674–679; *Development* **2004**, *8*, 674–679.
- [13] J. J. Gilman, *Chemistry and Physics of Mechanical Hardness, Vol. 5*, John Wiley & Sons: New York City, **2009**.
- [14] a) G. Y. Chin, L. G. Van Uitert, M. L. Green, G. Zydzik, *Scr. Metall.* **1972**, *6*, 475–479; b) T. T. Rao, D. B. Sirdeshmukh, *Cryst. Res. Technol.* **1991**, *26*, K53–K59; c) D. B. Sirdeshmukh, K. G. Subhadra, K. K. Rag, T. T. Rao, *Cryst. Res. Technol.* **1995**, *30*, 861–866; d) D. B. Sirdeshmukh, P. G. Krishna, K. G. Subhadra, *J. Mater. Sci.* **2003**, *38*, 2001–2006.
- [15] D. B. Sirdeshmukh, L. Sirdeshmukh, K. G. Subhadra, *Alkali Halides: a Handbook of Physical Properties, Vol. 49*, Springer Science & Business Media: Berlin, **2013**.
- [16] E. A. Neppiras, *Phys. Rep.-Review Section of Physics Letters* **1980**, *61*, 159–251.
- [17] a) O. de Vegt, H. Vromans, W. Pries, K. V. Maarschalk, *Int. J. Pharm.* **2006**, *317*, 47–53; b) O. de Vegt, H. Vromans, J. den Toonder, K. V. Maarschalk, *Powder Technol.* **2009**, *191*, 72–77.
- [18] Y. T. Didenko, K. S. Suslick, *Nature* **2002**, *418*, 394–397.
- [19] a) K. S. Suslick, J. J. Gawienowski, P. F. Schubert, H. H. Wang, *J. Phys. Chem.* **1983**, *87*, 2299–2301; b) K. S. Suslick, D. A. Hammerton, R. E. Cline, *J. Am. Chem. Soc.* **1986**, *108*, 5641–5642.
- [20] a) Ref. [5]; b) E. B. Flint, K. S. Suslick, *Science* **1991**, *253*, 1397–1399.
- [21] K. S. Suslick, G. J. Price, *Annu. Rev. Mater. Sci.* **1999**, *29*, 295–326.
- [22] S. Majumdar, P. S. Kumar, A. B. Pandit, *Ultrason. Sonochem.* **1998**, *5*, 113–118.
- [23] a) M. Kass, *Mater. Lett.* **2000**, *42*, 246–250; b) S.-H. Chu, S. H. Choi, J.-W. Kim, G. C. King, J. R. Elliott, in *Smart Structures and Materials 2006: Smart Electronics, Mems, Biomems, and Nanotechnology, Vol. 6172* (Ed.: V. K. Varadan), **2006**, pp. A1720–A1720; c) G. J. Price, M. F. Mahon, J. Shannon, C. Cooper, *Cryst. Growth Des.* **2011**, *11*, 39–44.
- [24] A. V. Potapov, C. S. Campbell, *Powder Technol.* **1997**, *93*, 13–21.
- [25] a) E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Sausalito, CA, **2006**; b) K. A. Dill, S. Bromberg, *Molecular Driving Forces*, 2 ed., Garland Science New York, **2011**.
- [26] a) N. Soga, *J. Non-Cryst. Solids* **1985**, *73*, 305–313; b) C. C. Yuan, X. K. Xi, *J. Appl. Phys.* **2011**, *109*.
- [27] M. Gent, M. Menendez, J. Torano, S. Torno, *Powder Technol.* **2012**, *224*, 217–222.

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