Microhardness studies of sulfamic acid single crystal

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Abstract. Vicker's microhardness study of (100), (010) and (001) faces of a non-linear optical crystal sulfamic acid have been reported. Single crystals of sulfamic acid have been grown by slow evaporation method. The load dependence of the Vickers microhardness of sulfamic acid crystal were investigated and analyzed from the stand point of various theoretical models. Crystal samples in a, b and c-axes exhibit reverse indentation effect which is best described by Meyer’s law, Hays-Kendall’s approach and proportional specimen resistance (PSR) models. The negative values of load dependent quantities in Hays-Kendall’s approach and PSR model suggest that the origin of indentation size effect is associated with the process of relaxation of indentation stresses.

1. Introduction

The wide range of industrial applications of the salts of sulfamic acid (NH\(_3\)SO\(_3\)) necessitates a thorough study of their various physical properties in the crystalline state. The crystal structure of sulfamic acid was reported to be orthorhombic with lattice parameters a=8.066, b=8.115 and c=9.255\(\text{Å}\) and have space group Pbca [1]. It has been suggested that it exist as a zwitterion, NH\(_3\)^+SO\(_3^-\), in the solid state [1, 2] and have nonlinear optical properties [3]. The elastic properties and thermal expansion of sulfamic acid and its sulfamates was reported by Haussuhl and Haussuhl [4]. Sulfamic acid undergoes a single stage irreversible endothermic transition at 448 K, where decomposition starts and the material was fully decomposed at 477 K [3]. In an earlier study we reported the dc electrical conductivity anomalies near 340 K and around 410 K in this crystal along a,
b and c-axes and these anomalies are attributed as due to a phase transition and the onset of the thermal decomposition respectively [5]. Differential scanning calorimeter and differential thermal analysis also supported the possible phase transition near 340K [5]. Ramesh et al [6] reported the dielectric constants of sulfamic acid crystal in the frequency range 10 - 103 Hz along with the Micro-Raman spectrum. The dielectric behavior was also studied by Lenin et al. [7].

One of the important properties of any device material is its mechanical strength, represented by its hardness [8]. The fastest and simplest type of mechanical testing is hardness measurement. Various other mechanical properties of the materials such as toughness, brittleness, yield strength, etc. have specific correlation with hardness [9-11]. Among the different testing methods, the Vickers hardness test method is more commonly used. The microhardness have been measured on the a, b and c-axes of sulfamic acid crystals at room temperature in the load region (5 to 100 g) in steps of 5 gm, where hardness is found to be a function of indenter load. The Meyer index otherwise known as the work-hardening exponent is computed using least squares fit analysis for different load regions and the results are discussed.

2. Experimental

Single crystals of sulfamic acid have been grown by slow evaporation method from an aqueous solution at 308 K with threefold recrystallization from distilled water. Transparent crystals of size 33 × 30 × 20 mm with good optical quality are obtained after a period of 60 -70 days. The grown crystals were examined by X-ray diffraction analysis. The powder diffraction pattern of the sample crystal is agreed well with that reported in the literature [JCPDS file No. 74-0342]. The natural faces of the crystal are identified by measuring the interfacial angle of the crystal and comparing it with calculated angles. Bulk samples have been cut into required thickness using a slow speed diamond wheel saw (MTI Corp. USA). The indentations were performed along a, b and c-axes at a very slow rate and for all indentations; care was taken to see that the rate was nearly the same. The indentation mark was square in shape. The diagonals of indentation mark were measured using micrometer eyepiece. The indentations using Vickers’ pyramidal diamond indenter were made at different loads ranging from 1 to 100 gm. Indentations were carried out in the low load region at different sites such that the distance between any two indentations was greater than three times the diagonal length, in order to avoid any mutual influence of the indentations. The measurements were made at room temperature and the time of indentation was kept at 10 sec throughout the work. Subsequent impressions were made after a time lapse of 10 min. to allow for any elastic recovery. The two diagonals of the indentation left in the surface of the crystal after removal of the load were measured using a micrometer eyepiece and their average length was calculated. The Vickers hardness is defined as the ratio of applied load to the pyramidal contact area of indentation and it is calculated as

\[ H_V = 1.8544 \left( \frac{P}{d^2} \right) \text{kg/mm}^2 \]

Where \( H_v \) = Vickers’ microhardness in Kg/mm², \( P \) = Applied load in gm, \( d \) = Mean diagonal length of the indentation mark in µm. The indentation mark is geometrically similar whatever be its size. This would imply the hardness to be independent of load. However, this is not the case and except for loads exceeding about 200 gm, in general, the measured hardness value has been found to depend on load in almost all cases and hence the hardness values measured in the low load region, are known as microhardness values. Though, the limit load is not sharply defined, practically the hardness may achieve a constant value for loads in the range 20–50 gm and beyond, depending on the material [12].

3. Results and discussions

3.1. Load variation of hardness

The variation of microhardness with applied indentation test load is shown in figure 1. The plots indicate clearly that the hardness varies with load in a complex manner. Starting from smallest load used, the hardness increases up to a load of about 50 gm. Beyond 50 gm., it reaches saturation. In
general the hardness varies considerably in the low load region as the work hardening capacity and elastic recovery of a particular material are dependent on the load, type of surface receiving the load, and the depth to which the surface is penetrated by the indenter. For example, the low load hardness behavior in the case of silicon single crystal has been explained on the basis of elastic recovery and piling up of material around the indentation mark [13]. Both the magnitude of work hardening and the depth to which it occurs depend on the properties of the material and are the greatest for soft metallic materials which can be appreciably work hardened. Since the penetration depth at high loads is usually greater than that of the work hardened surface layer, the hardness value at high loads will be representative of the undeformed bulk of the material and hence independent of load [12].

The apparent microhardness of solids depends on the applied indentation test load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the microhardness with increasing applied test load, i.e. with increasing indentation size [14-18]. In contrast to the above normal ISE, a reverse type of indentation size effect (called reverse ISE), where the apparent microhardness increases with increasing applied test load, is also known [19-21].

It is observed that the sulfamic acid crystal exhibited reverse indentation size effect (ISE), in which an increase in the apparent microhardness with increasing indentation size. The variation of microhardness with increasing indentation size is shown in figure 2. Although the ISE has been explained by dislocation behaviour during indentation [14, 22], the reverse ISE has been explained in terms of the existence of a distorted zone near the crystal medium interface, effects of vibration, and indenter bluntness at low loads [19, 21].

3.2. log P vs log d plots
In order to describe the ISE behaviour of materials, several models for the relationship between applied indentation test load and indentation diagonal length have been reported in the literature. The most common explanation of the ISE found in the literature is directly related to the intrinsic structural factors of the test material [23, 16-18]. According to this theory, in order to analyze the ISE in the hardness testing, one needs to fit the experimental data according to Meyer's law, which correlates the applied load P and the resulting indentation size d with each other:

\[ P = Ad^n \]

where the exponent n, called as the Meyer number (or index), is a measure of the ISE and A is a constant. The values of n and A of above equation may be obtained from the plots of log P against log d. Figure 3 shows the log P vs log d plots. The ISE is usually related to the deviation of the n value
from 2, for n equal to 2 is the absence of an ISE or the hardness is independent of the applied test load [24]. When n > 2, there is the reverse ISE behaviour. The graph is more linear for loads greater than 50 gm. So we consider the best fit plots for the data at P≥ 50 gm. The values obtained for the Mayer’s index are 2.1212, 2.099, and 2.176 for a, b and c axis respectively, for loads greater than 50 gm. The experimental data show that value of n is always greater than 2. This reveals that the crystal samples exhibit reverse indentation size effect. Onitsch [25] and Hanneman [26] from careful observations on various materials pointed out that n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. The 'n' values observed in the present studies are above 1.6 suggesting that Sulfamic acid crystal is a soft material.

3.3. Hays and Kendall’s approach
According to this approach [27] there is a threshold load W necessary to initiate permanent deformation, and the load dependence of hardness may be expressed by

\[ P = W + A_1d^2 \]

where W is the minimum load to initiate plastic (permanent) deformation, \( A_1 \) is a load-independent constant. The values of W and \( A_1 \) may be calculated by plotting the experimental P(d) data as P against \( d^2 \) plots. Figure 4 shows the plots of P against \( d^2 \).

| Axes   | Load range | \( A_1 \) (g/\( \mu m^2 \)) | W (g)   |
|--------|------------|-----------------------------|--------|
| a-axis | Low P      | 0.08079                     | -104.63|
|        | High P     | 0.02801                     | -4.23  |
| b-axis | Low P      | 0.08983                     | -138.73|
|        | High P     | 0.02525                     | -3.424 |
| c-axis | Low P      | 0.05066                     | -64.35 |
|        | High P     | 0.03183                     | -38.65 |
It is observed that the plots of $P$ against $d^2$ for $a$, $b$ and $c$ axes are very similar and consists of two linear parts for $d < d_c$ and $d > d_c$, respectively. The calculated values of $W$ and $A_1$ for different samples are listed in Table 1. It may be noted from Table 1 that the value of $W$ is negative for all loads. The negative values of $W$ express the reverse ISE. This suggests that the crystal samples exhibit reverse indentation size effect. In the range of $d < d_c$ there are high negative values of $W$ for $a$- and $b$-axes. Very high negative values of $W$ suggest that a sudden increase in the value of $H_v$ for $d < d_c$ does not occur by this mechanism [28].

3.4. Proportional specimen resistance model

Several workers [16-17, 29-30] have proposed that the normal ISE behaviour may be described by the relation

$$P = ad + bd^2$$

where the parameter $a$ characterizes the load dependence of hardness and $b$ is a load-independent constant. The term $ad$ has been attributed to the specimen surface energy [29-30], the deformed surface layer, the indenter edges acting as plastic hinges, and the proportional specimen resistance [16-17]. The constants $a$ and $b$ may be obtained from the plots of $P/d$ against $d$ for the samples. Figure 5 shows the plots of $P/d$ against $d$ for $a$, $b$ and $c$-axes

![Figure 5. Plots of $P/d$ against $d$ for $a$, $b$ and $c$-axes](image)

It should be noted that $a > 0$ results in the appearance of normal ISE in which $H_v$ decreases with an increase in indentation diagonal $d$. However, when $a < 0$ a reverse ISE, in which $H_v$ increases with an increase in indentation diagonal $d$, is produced. According to Li and Bradt [16], the value of $a$ is positive when elastic surface stresses are compressive. This leads to a reduction in the value of $d$ upon unloading. This implies that the value of $a$ is negative when surface stresses are tensile, which lead to a relaxation of these surface stresses introduced by indentation. There are several cases of the occurrence of normal and reverse ISE for different materials [14]. It was suggested that the value of $a$ can be negative both due to the development of indentation cracks as well as motion of dislocations in the form of dislocation rosettes.

It was observed that, the $[P/d]$ vs. (d) plots for $a$, $b$ and $c$-axes are very similar and consists of two practically linear parts for $d < d_c$ and $d > d_c$, respectively. Values of $a$ and $b$ for different samples are calculated and is listed in Table 2. It should be noted that, as expected for reverse ISE, the values of $a$ are negative. In the case of reverse ISE similar observations were made earlier for other materials [14]. According to Li and Bradt [16] when elastic surface stresses are compressive the sign of $a$ is positive. The negative values of $a$ suggest that the surface stresses are tensile, which implies that reverse ISE is
associate with the relaxation of these surface stresses introduced by indentation. However, in the present case of sulfamic acid crystals relaxation of the surface stresses occurs as a result of development of indentation cracks.

| Axes | Load range | a (g/µm) | b(g/µm²) |
|------|------------|----------|----------|
| a-axis | Low P | -5.24 | 0.14539 |
|       | High P | -0.1656 | 0.02959 |
| b-axis | Low P | -6.44 | 0.16404 |
|       | High P | -0.1284 | 0.02642 |
| c-axis | Low P | -3.08 | 0.08691 |
|       | High P | -0.2193 | 0.0628 |

4. Conclusion
The growth and microhardness study of sulfamic acid crystal are carried out. The grown crystal was almost defect-free and was identified by X-ray diffraction technique. Vickers microhardness has been studied along a, b and c-axes and the results obtained were on predicted lines. The values of microhardness show an increase with increasing the test load. This phenomenon gives the idea of reverse ISE. The values of Meyer’s index obtained for a, b and c- axes of the crystal are also in agreement with the above observation. Analysis of the experimental data on hardness as a function of indentation size from the stand point of Hays-Kendall’s approach and the proportional specimen resistance model revels that these models satisfactorily explain the reverse ISE on the different axes of sulfamic acid crystal.

References
[1] Kanda FA and King AJ 1951 *J Am Chem Soc* 73 2315
[2] Sass RL 1960 *Acta Cryst* 13 320
[3] Valluvan R, Selvaraju K and Kumararaman S 2006 *Mat Chem Phys* 97 81
[4] Haussuhl E and Haussuhl S 1995 *Zeitschrift fur kristallographie* 210 269
[5] Kumar AS, Varughese G, Iype L, Rajesh R, Joseph G and Louis G 2010 *Cryst Res Technol* 45 879
[6] Babu RR, Sethuraman K, Vijayan N, Gopalakrishnan R and Ramasamy P 2007 *Mat Letts* 61 3480
[7] Lenin M, Balamurugan N and Ramasamy P 2007 *Cryst Res Technol* 42 39
[8] Subhadra KG, Rao KK and Sirdeshmukh D B 2000 *Bull Mater Sci* 23 147
[9] Bergner F, Bergmann U, Schaper M, Hammer R and Jurisch M 2001 *Material Prüfung* 25 117
[10] Lal B, Bamzai KK and Kotru P N 2003 *Materials Chem & Phys* 78 202
[11] Wooster W A 1953 *Rep Prog Phys* 16 62
[12] Desai C F, Maunik J, Soni P H and Pandya GR 2009 *J Mater Sci* 44 3504
[13] Walls MG, Chaudhri MM and Tang TB 1992 *J Phys D Appl Phys* 25 500
[14] Sangwal K and Surowska B 2003 Mat Res Innovat 7 91
[15] Bull SJ, Page TF and Yoffe E H 1989 Phil Mag Lett 59 281
[16] Li H and Bradt RC 1993 J Mater Sci 28 917
[17] Li H, Han YH and Bradt RC 1994 J Mater Sci 29 5641
[18] Jain A, Razdan AK, Kotru P N and Wanklyn B M 1994 J Mater Sci 29 3847
[19] Berzina I G, Berman I B and Savintsev P A 1965 Kristallografiya 9 483
[20] Westbrook J H 1967 Environment-Sensitive Mechanical Behaviour In: Westwood ARC, Stoloff NS (eds) (New York: Gordon-Breach) p 247
[21] Hanneman R E and Westbrook J W 1968 Phil Mag 18 73
[22] Gane N and Cox J M 1970 Phil Mag 22 881
[23] Mott B W 1956 Microindentation Hardness Testing (London: Butter worths)
[24] Pal T and Kar T 2003 Mater Sci Eng A 354 331
[25] Onitsch E M 1947 Mikroskopie 2 131
[26] Hanneman M 1941 Metallurgia Manchu 23 135
[27] Hays C and Kendall E G 1973 Metallography 6 275
[28] Sangwal K and Klos A 2005 Cryst Res Technol 40 429
[29] Frohlich F, Grau P and Grellmann W 1977 Phys Stat Sol (a) 42 79
[30] Michels B D and Frischat G H 1982 J Mater Sci 17 329