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Vickers microhardness studies on solution-grown single crystals of magnesium sulphate hepta-hydrate

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Abstract

A Vickers microhardness study has been carried out on (1 0 0) and (0 1 0) faces of solution-grown single crystals of magnesium sulphate hepta-hydrate ($MgSO_4{\cdot}7H_2O$) over a load range of 10–80 g. The Vickers hardness numbers (H_v) are found to decrease initially with increase in load and then appear to level-off. The (1 0 0) face is the softest one. The Meyer index 'n' of the two faces is less than 2 as expected theoretically if the particular crystal system belongs to the soft material category. Neither Kick's law nor Hays and Kendall's law can fully explain the nonlinear variation of microhardness with load. Instead, preference is given to Li and Bradt's proportional specimen resistance (PSR) model. The elastic stiffness coefficient, c_{11}, has also been calculated using Wooster's empirical relation from the hardness data and it shows reasonable agreement with a reported value. A hardness anisotropy for both planes has been observed in accordance with the orientation of the crystallographic planes.

Keywords: Magnesium sulphate hepta-hydrate; Solution growth; Vickers microhardness; Hardness anisotropy

1. Introduction

Magnesium sulphate is a chemical compound having immense applications in several industries (textile, pharmaceutical, sucrose, etc.). It is one of the important fertilizers supplying the most important element, magnesium, to crops. Moreover, it has wide applications in the medical fields. Magnesium sulphate is also well known in chemical industries and it has been used as a raw material for manufacturing various chemicals containing magnesium. It has also wide applications in luminescence [1] and dosimetric [2] studies. Magnesium sulphate hepta-hydrate ($MgSO_4{\cdot}7H_2O$) is an important member of a group of hepta-hydrated sulphates with general formula $RSO_4{\cdot}7H_2O$ (R = Mg, Ni, Zn) [3]. $MgSO_4{\cdot}7H_2O$ (MS) has two modifications: α and β forms existing above and below 800 °C, respectively [1]. β-$MgSO_4{\cdot}7H_2O$ crystallizes in an orthorhombic disphenoidal structure with a tetra molecular unit cell of dimensions $a = 11.887$, $b = 12.013$ and $c = 6.861$ Å having a space group $P2_12_12_1$ [4]. $MgSO_4{\cdot}7H_2O$ is among the most interesting inorganic substances frequently chosen for studies of the crystal growth kinetics over last few decades. Studies of their linear growth rate and the effects of solution flow velocity, temperature, additives on their absolute growth rate have been the subject matter of many investigations [5–10]. Moreover, extensive research works have been done to study the morphological behaviour [11] and physical properties [12] of MS crystals. But to our knowledge, no works on mechanical properties of this crystal has been reported till to-date. Of all the well-known techniques to assess this property of a material, indentation hardness testing is one in most widespread use. The measurement of hardness is very important as far as the fabrication and failures of devices concerned. In continuation of our earlier work on pure ammonium sulphate (AS) [13], mixed ammonium–potassium sulphate [14], pure sodium sulphate [15], we will present here our recent results and interpretation on microhardness studies on solution grown single crystals of magnesium sulphate hepta-hydrate.

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2. Experimental procedure

Single crystals of MS have been grown at an ambient temperature of 30 ± 1 °C, by slow evaporation method. A supersaturated solution of MS has been prepared at 30 °C using the predetermined solubility data. The solution is then warmed slightly and stirred well to avoid any spurious nucleation. The pH of the solution is maintained between 4 and 5 adding few drops of concentrated sulphuric acid. The solution is filtered and kept in partly covered high walled crystallizing dishes. Single crystals of MS having typical growth morphology have been harvested nearly after 3 weeks. The typical growth habit of the crystal is shown in Fig. 1.

The mechanical characterization of MS crystals has been done by microhardness testing at room temperature. Transparent MS crystals free from cracks having approximate dimension of 10 mm × 5 mm × 2 mm, with flat and smooth faces, are chosen for the static indentation tests. Plates parallel to different crystallographic directions having few mm of thickness are cut from the as-grown crystals and polished gently with 50:50 ethanol–water solution. No crystallographic faces other than (0 1 0) and (1 0 0) faces are well developed to do the indentation tests and so our microhardness studies have been confined to the earlier mentioned two faces. The crystal has been mounted properly on the base of the microscope. Now the selected faces have been indented gently by the loads varying from 10 to 80 g for a dwell period of 10 s using Vickers diamond pyramid indenter attached to an incident ray research microscope (Carl-Zeiss, Jenavert, Germany). The indented impressions are approximately square in shape. The shape of the impression is structure dependent, face dependent and also material dependent. The length of the two diagonals has been measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average is found out. For a particular load at least five well-defined impressions have been considered and the average of all the diagonals (d) has been considered. The Vickers hardness numbers (H_v) have been calculated using the standard formula:

$$H_v = \frac{1.8544P}{d^2} \quad (1)$$

where P is the applied load in kg, d in mm and H_v is in kg/mm^2. Crack initiation and materials chipping become significant beyond 80 g of the applied load so hardness test cannot be carried out above this load. We have also calculated elastic stiffness constant (c_{11}) following Wooster's empirical relation [16] as

$$c_{11} = H^{7/4}. \quad (2)$$

We have also tried to measure the hardness anisotropy with the crystal orientation. As indentation initiates plastic deformation in a crystal, which is highly directional in nature, the hardness measurement may be a function of the orientation of the indented crystal. Thus, any anisotropic effect shown by the size of the indentation mark will be reflected in hardness number. In order to study the hardness anisotropy present in different crystallographic faces on MS crystals, the crystal is initially mounted on the stage on the microscope properly and indented. The initial position (0°) of the index line has been set when one of the diagonals of the indented impression has been parallel to ⟨1 0 0⟩ direction. The stage of the microscope then has been rotated keeping the indenter fixed and H_v has been measured at every 15° interval.

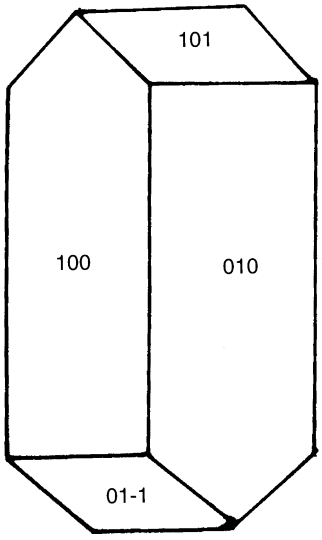

Fig. 1. Typical growth morphology of MS crystal.

3. Results and discussion

Fig. 2 shows the variation of H_v as a function of applied loads ranging from 10 to 80 g for (0 1 0) and (1 0 0) faces. It is clear from the figure that H_v of the two faces initially decreases with increase in load (from 10 to 50 g) and then appears to level off. This is known as load independent hardness and here its value is found to be approximately as 44 and 33 kg/mm^2 for (0 1 0) and (1 0 0) faces, respectively. H_v for (0 1 0) plane attains saturation at a rather large value than that for (1 0 0) plane. Thus, the (1 0 0) plane is found to be softer than the (0 1 0) plane. The variation of hardness in different crystallographic planes is due to crystal orientation-dependent plasticity, which generally varies in different crystallographic directions. Such a phenomenon of dependence of microhardness of a solid on the applied load at low level of testing load is known as indentation size effect (ISE). The observed decrease in hardness with increasing load is usually termed as normal ISE, which was also observed earlier by other workers [17–19]. The errors on H_v have been estimated for each P/d^2 using the formula:

$$\Delta H_v = 1.8544\left[\left\{\left(\frac{1}{y}\right)\Delta P\right\}\right]^2 + \frac{P^2}{y^4}(\Delta y)^2]^{1/2} \quad (3)$$

where $y = d^2$ and $\Delta y = 2d\,\Delta d$, ΔP is the experimental error on P [20]. ΔH_v's are found to be ±0.0008 and ± 0.0009 g/μm^2