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Vickers microhardness studies on cadmium mercury thiocyanate (CMTC) single crystals grown in silica gel

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Abstract

Vickers microhardness study was carried out on the (110) face of the gel-grown cadmium mercury thiocyanate (CMTC) single crystal, subjected to the loads 10, 25 and 50 g. The measurements were made at room temperature with the indentation time as 10 s. Vickers hardness number Hv was calculated and it is found to increase with the applied load. Mayer's index number '*n*' and elastic stiffness constant were calculated. The anisotropy of the crystal is also studied. The results are discussed in detail.

Keywords: Vickers microhardness; Hardness anisotropy

1. Introduction

Nonlinear optical materials are of much interest because of their potential applications over a wide range, due to their efficiency of frequency conversion. Cadmium mercury thiocyanate abbreviated as CMTC is a semi-organic bimetallic thiocyanate complex that exhibits nonlinear optical property. It crystallizes in a noncentrosymmetric space group $I\overline{4}$ with no color and possess high thermal stability [1]. It belongs to tetragonal crystal system with lattice parameters $a=b=11.487$ Å & $c=4.218$ Å. CMTC is an excellent second-order nonlinear optical material for the second harmonic generation (SHG) of Nd:YAG laser radiation of wavelength 1064 nm [2,3]. Intracavity-frequency-doubling of a 946 nm Nd:YAG laser with CMTC crystal has been reported by Changqiang Wang et al. [4] and blue-violet light generation with GaAlAs diode laser at room temperature has been realized by Yuan et al. [5]. Since it undergoes decomposition before melting, the only of getting these crystals is from solution. CMTC single crystals were obtained from solution by solvent evaporation method by different researchers and several characterizations had been carried out. Growth of CMTC single crystals in silica gel had been reported by Blank [6] using the reagents mercury(II) nitrate, cadmium nitrate, ammonium thiocyanate and sodium thiocyanate. Tiny crystals of size 2–3 mm were obtained and chemical and thermal analyses had been carried out. Our work was concentrated on the growth of CMTC single crystals in silica gel using the reagents mercury(II) chloride, cadmium chloride and ammonium thiocyanate. Colorless transparent crystals of size 10 mm × 3.1 mm × 3.2 mm have been obtained. Hardness measurement is very important for device fabrications. Among the different testing methods, the Vickers hardness method is more commonly used. Many researchers have investigated the mechanical properties of different crystals. Vickers microhardness studies on solution-grown single crystals of magnesium sulphate hepta-hydrate have been reported by Susmita Karan et al. [7] and Kunjomana et al. [8] have studied the microhardness of GaTe whiskers. To our knowledge there is no study available, on the mechanical characterization of CMTC single crystals. The present investigation covers the Vickers microhardness measurement of gel-grown CMTC single crystals at room temperature considering the (110) plane.

2. Experimental

2.1. Crystal growth

Single crystals of CMTC have been obtained from silica gel, by single diffusion method. It was grown in an acidic medium

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of pH 3.4. The reaction between cadmium chloride, mercury(II) chloride and ammonium thiocyanate in gel medium resulted in the growth of CMTC single crystals.

The reaction that takes place is given below.

$$CdCl_2 + 4\ NH_4SCN + HgCl_2 \rightarrow CdHg(SCN)_4 + 4NH_4Cl$$

Mercury(II) chloride and ammonium thiocyanate together were taken as the inner reagent and cadmium chloride was added on to the top of the gel as an outer reagent.

As reported by Heinz K. Henisch, stock solution of sodium meta silicate was prepared by adding 244 grams of sodium meta silicate ($Na_2SiO_3\ 9H_2O$) to 500 ml of distilled water [9]. By adjusting the pH of the stock solution to 3.4 with ExcelaR grade glacial acetic acid of purity 99.8 and using the above mentioned inner and outer reagents, colorless transparent crystals of size 10 mm × 3.1 mm × 3.2 mm were obtained within 30 days. The experiment was carried out at an ambient temperature of about 30 °C. The as-grown CMTC single crystal and its morphology are shown in Fig. 1.

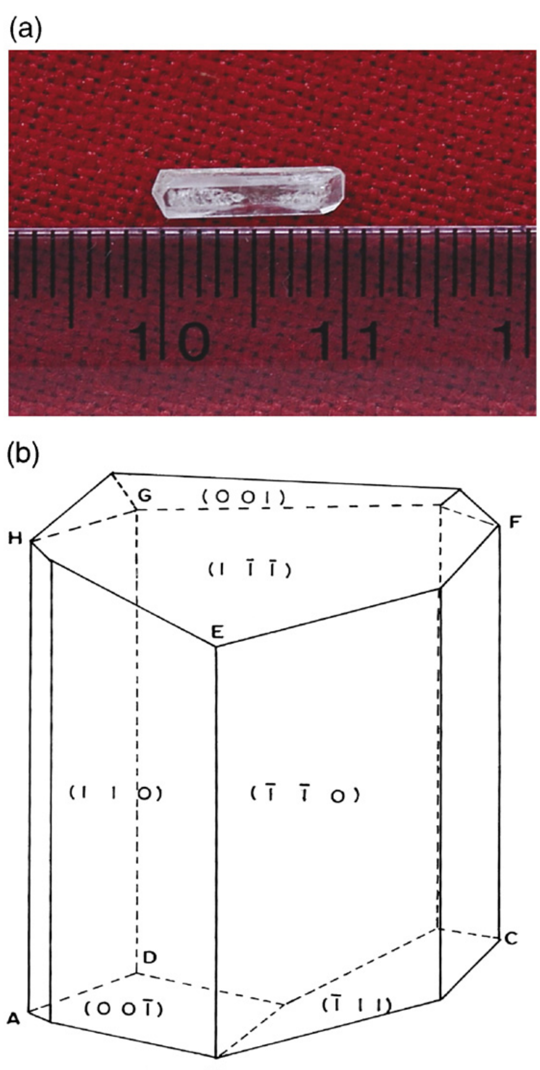

Fig. 1. (a) As-grown and (b) Morphology of gel-grown CMTC crystal.

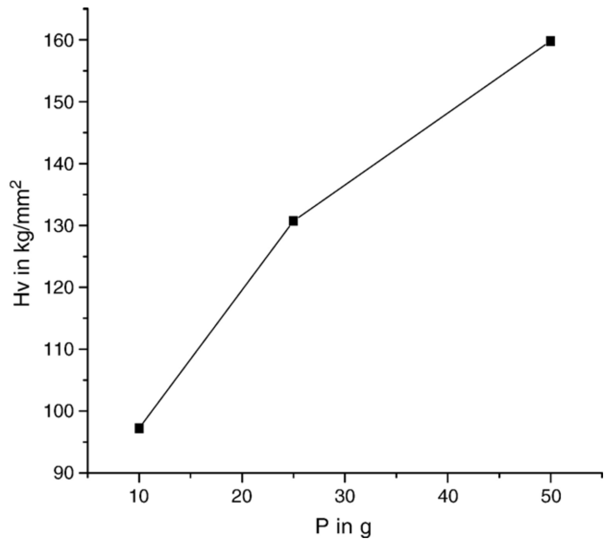

Fig. 2. Plot of Vickers hardness number vs. load.

2.2. Microhardness measurements

Gel-grown CMTC crystals with flat and smooth faces, microscopically free from signs of any damage having approximate dimension of 5 mm × 3 mm × 3 mm were selected for indentation studies. Indentations were made on a selected crystal, using an MH-112 Vickers microhardness tester (Japan). The (110) surface of the selected crystal was polished gently with ethanol–water mixture (1:1 ratio), before carrying out the indentation procedure. The crystal was mounted properly on the base of the microscope and the selected face was indented gently by the loads 10, 25 and 50 g for a dwell period of 10 s using Vickers diamond pyramid indenter attached to an incident ray research microscope. The indented impressions were approximately square in shape. The shape of the impression is structure dependent, face dependent and also material dependent. The lengths of the two diagonals of the indentations were measured by a calibrated micrometer attached to the eye piece of the microscope after unloading and the average (d) is found out. The Vickers hardness number is computed using the formula

$$H_v = 1.8544\,P/d^2 \tag{1}$$

where H_v is the Vickers hardness number in kg/mm^2, P is the indenter load in kg and d is the diagonal length of the impression in mm.

Since crack initiation and material chipping became significant beyond 50 g of the applied load, hardness test could not be carried out above this load. Elastic stiffness constant is calculated using Wooster's empirical formula [10]

$$C_{11} = H_v^{7/4}. \tag{2}$$

We have also measured the hardness anisotropy, with the crystal orientation. The hardness measurement, as a function of the orientation of the indented crystal is important, since indentation initiates plastic deformation in a crystal, which is highly directional in nature. The anisotropic effect shown by the size of the indentation mark is reflected in hardness number. To