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Vickers Microhardness Study of Nonlinear Optical Single Crystals of Doped and Undoped S-Benzyl Isothiouronium Chloride

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The Vickers microhardness of the doped and undoped S-benzyl isothiouronium chloride single crystals was investigated using a Vickers microhardness tester at room temperature. It was observed that, up to an applied load of 15 g, the hardness of the crystals increases with an increase in load, and thereafter it is practically independent of the indentation load. Efforts are made to improve the hardness of S-benzyl isothiouronium chloride crystal by doping. It was found that all doped crystals possess greater hardness than the undoped crystals.

Keywords chemical analysis, material selection, mechanical testing

1. Introduction

The growth and structural, thermal, and NLO behaviors of s-BTC crystals have been studied and reported (Ref 1). A hardness study of the doped and undoped s-BTC crystals has been carried out and is reported for the first time. It is well known that microhardness (MH) is not only a mechanical characteristic routinely measured, but also it has been developed as a microstructural investigation method, due to the fact that MH is sensitive to structural parameters as well as to mechanical characterization parameters (yield stress, modulus of elasticity, some secondary relaxation transitions, etc.) (Ref 2, 3).

The hardness of a material is defined as the resistance it offers to the motion of dislocations, deformation, or damage under an applied stress (Ref 4). The general definition of indentation hardness, which relates to the various forms of indenters, is the ratio of the applied load to the projected area of indentation. Generally, the apparent hardness of the materials varies with applied load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the MH with increasing applied load (Ref 5-10). The decrease of MH with increasing applied load has been reported by various authors (Ref 11-14). In contrast to the ISE, a reverse type of indentation size effect (reverse ISE), where the MH increases with increasing applied load, is also known (Ref 15-17). Kotru et al. described the ISE with the help of a modified law of Hays and Kendall (Ref 14). Recently, Li et al. developed a proportional specimen resistance (PSR) model to explain the ISE. In this model, the two contributing factors to the ISE are the friction between the indenter facets and the test specimen and the elastic resistance of the test specimen (Ref 18).

This article reports result of hardness measurements aimed at improving the hardness of s-BTC crystals by various dopants.

2. Experimental

Single crystals of doped and undoped S-benzyl isothiouronium chloride were grown by slow evaporation at room temperature. For hardness measurements, transparent crystals with a thickness of 2 mm, free from visible inclusions or cracks, were selected. Diamond pyramid hardness measurements of all the crystals were performed with a digital microhardness tester, at room temperature for applied loads ranging from 5 to 25 g. The dwell time for each load was 10 s. Seven indentations at different locations of the specimen surfaces were taken for each load, and the average diagonal length of the indented impressions was calculated. The Vickers hardness value (Hv) was calculated from the following equation:

$$\mathrm{H}v = 1.8544\, P/d^2 \qquad \text{(Eq 1)}$$

where P is the applied load, d is the average diagonal length of the indented impressions, and 1.8544 is a constant, a geometrical factor for the diamond pyramid. The indenter gives geometrically similar indentations; hence, it follows that the measured hardness must be independent of the applied load. However, it has been well known that, for many engineering materials, the calculated microhardness are load dependent. The values of Hv for all crystals were determined according to Eq 1 and are plotted in Fig. 1 as a function of the applied indentation test load at room temperature.

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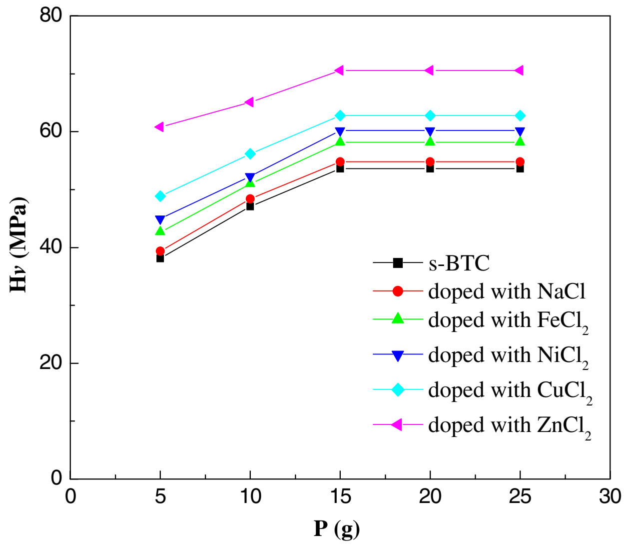

Fig 1 Vickers hardness number as a function of indentation load

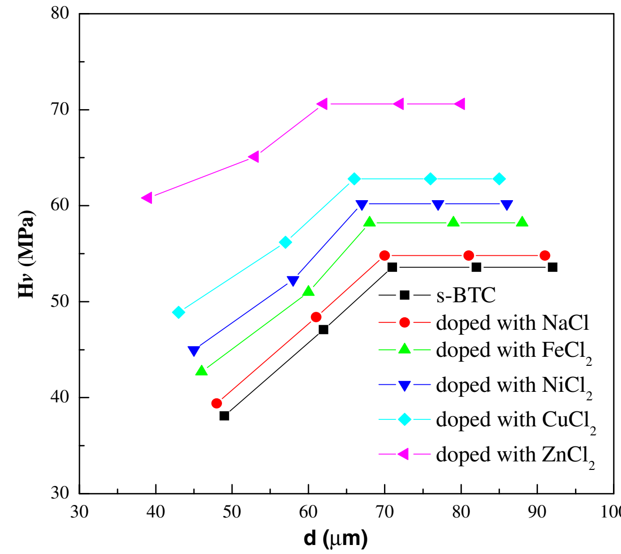

Fig 2 Microhardness against indentation diagonal d

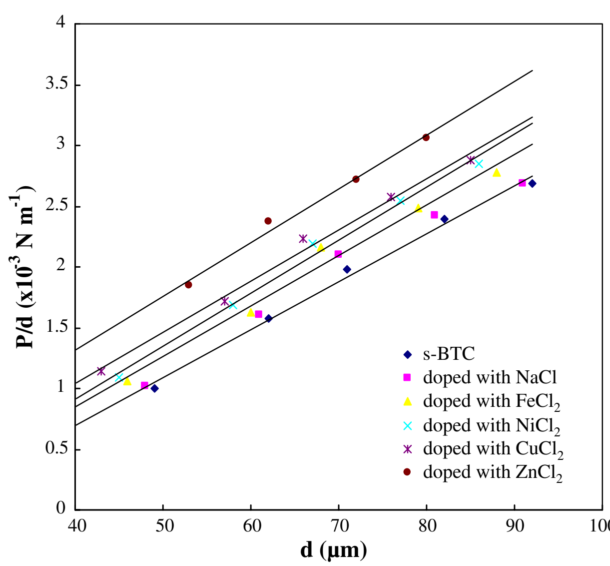

Fig 3 P/d plotted against d for tested samples

3. Results and Discussion

The variation of microhardness Hv with applied load for the doped and undoped S-benzyl isothiouronium chloride is illustrated in Fig. 1. For all crystals there is an increase in microhardness values up to 15 g load, after which saturation occurs with little increase in hardness with applied load. Above 25 g load, significant cracking occurs and further study was not possible. From Fig. 1, it is obvious that the undoped S-benzyl isothiouronium chloride crystal possesses low hardness compared with doped crystals. It is well known that, according to their periodical arrangement of elements, the physical and chemical properties vary gradually. Here, the hardness value increases gradually with increasing atomic number.

Figure 2 shows plots of microhardness of doped and undoped crystals against average indentation diagonal length d. The figure illustrates typical examples of the reverse ISE of all crystals. The theoretical model describes the ISE phenomena through the load-independent and load-dependent contributions represented by load-independent and load-dependent constants, respectively (Ref 18, 19). The load-independent constants are used to calculate the material hardness. Meyer's law (Ref 19) and indentation-induced cracking model (Ref 20) are the different ISE models that give load-independent constants with units different from conventional units of pressure. These models give suitable results only in a narrow range of indentation loads. It can be seen from Fig. 1 that Hv for all crystals attains saturation for high indentation test loads. This saturated value of Hv is consistent with the load-independent value of Hv. The classical Meyer's law is insufficient for the description of experimental data at the high load regions. Therefore, it cannot be used to calculate load-independent hardness.

Recently many researchers (Ref 21-23) showed that the PSR model is suitable for analyzing both the load independence and the saturation of Hv. According to the PSR model, the indentation test load P is related to indentation size d as follows:

$$P = a_1 d + a_2 d^2 \qquad \text{(Eq 2)}$$

The parameter a_1 characterizes the load dependence of hardness and a_2 is a load-independent constant. The constants a_1 and a_2 of Eq 2 may be obtained from the plots of P/d against d for the samples. The slope gives the value of P/d^2 which, when multiplied by the Vickers conversion factor 1.8544, gives the value of the load-independent microhardness, H_o. Typical examples of such plots are shown in Fig. 3, while the calculated values of a_1 and a_2 are listed in Table 1.

From Table 1, it can be seen that there is no significant change in the a_2 parameter of the doped crystals. The value of a_1 is directly proportional to Young's moduli and a_1/a_2 may be considered as a measure of the residual stress, and these are connected with defects (Ref 18). By contrast, the a_1 parameter is known as a measure of surface effects during microhardness indentation. From Table 1, it is obvious that the a_1 parameter increases according to the atomic number of the doped element. An increasing tendency of the calculated Hv with various dopants may be due to defects caused by crystallization.

Table 1 Regression analysis of experimental data according to Eq 3

Sample	$a_1 \times 10^{-4}$, N μm^{-1}	$a_2 \times 10^{-5}$, N μm^{-2}	H_o, MPa	Residual stress, μm
s-BTC	5.19	2.35	43.58	22.08
Doped with NaCl	5.64	2.38	44.16	23.69
Doped with $FeCl_2$	5.97	2.40	44.58	24.87
Doped with $NiCl_2$	6.36	2.47	45.79	25.75
Doped with $CuCl_2$	6.59	2.51	46.54	26.25
Doped with $ZnCl_2$	6.71	2.53	46.91	26.52

4. Conclusion

In conclusion, the results in the present study for doped and undoped crystals of s-BTC are reported in the first time. At lower loads there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layer. At higher loads, the microhardness shows a tendency to saturate. Beyond the load of 25 g, significant cracking occurs, which may be due to the release of internal stresses generated locally by indentation. Each crystal exhibits a significant ISE with indentation load. ISE is described by the PSR model of Li and Bradt. The increasing value of microhardness makes the crystals harder. Finally, the microhardness measurements can be used to explain the mechanical behaviors like Young's modulus and residual stress of the crystals.

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