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MICROINDENTATION HARDNESS OF $SrLaAlO_4$ and $SrLaGaO_4$ SINGLE CRYSTALS

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The Vickers microhardness of the (100) and (001) planes of $SrLaAlO_4$ and $SrLaGaO_4$ single crystals was investigated using a PMT-3 hardness tester up to an applied load of 100 g. It was observed that, up to an applied load of 50 g, the hardness of the crystals increases with an increase in load and thereafter it is practically independent of the indentation load. The experimental data were analysed using Hays-Kendall and Li-Bradt models to obtain load-independent hardness of the crystals. The results showed that: (1) for crystals of a particular orientation, the load-independent hardness obtained by Li-Bradt model is higher by a factor of about 4/3 than that predicted by Hays-Kendall model, (2) the load-independent hardness of the (100) plane is higher than that of the (001) plane for both SLA and SLG crystals, but the hardness anisotropy is more pronounced in SLA than SLG crystals, and (3) the load-independent hardness of a sample of a particular orientation practically does not depend on indenter orientation on the indented sample.

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1. Introduction

$SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) belong to groups of compounds with the general chemical formula $ABCO_4$, where A denotes Sr, B transition-metal elements (for example, La here) while C denotes Al, Ga or some other transition-metal element of similar properties [1]. Most of the $ABCO_4$ compounds (e.g. SLA and SLG) crystallise in the tetragonal structure but some compounds crystallising in the orthorhomic structure are also known. It is believed that Sr and La ions are statistically distributed at lattice sites in the a-b plane of the unit cell. Good quality SLA and SLG single crystals are obtained by Czochralski method and are used as substrates for the deposition of high temperature superconducting thin films [1]. At ordinary temperatures the crystals are brittle [1].

Pajaczkowska and Gloubokov [1, 2] reported the microhardness of the (100) and (001) planes of SLA and SLG crystals at a constant load, but they did not give details of the applied load and indenter orientation on the indented plane of the samples. Apart from the above work there is practically no information on the microhardness measurement of these crystals. However, it is well known that the apparent (i.e. measured) microhardness of solids depends on the applied indentation test load. This phenomenon is known as the indentation size effect (ISE). Usually, ISE involves a decrease in the apparent microhardness with increasing applied test load (normal ISE) but a reverse ISE involving an increase in microhardness with increasing applied test load is also known. The literature on normal and reverse ISE may be found in refs. [3, 4].

The aim of this paper is to study the load dependence of microhardness of the (100) and (001) faces of SLA and SLG crystals and to determine their load-independent hardness, using theoretical models.

2. Experimental

SLA and SLG single crystals for microindentation hardness tests were grown on <110> oriented seeds by Czochralski method [1]. The grown crystals were cylindrical boules with the (001) facets along their length. Parallelepiped-shaped plates of dimensions 10 mm × 7-8 mm × 0.5-1.0 mm with the (100) and (001) orientations of their surfaces for microhardness testing were cut from the cylindrical boules, and one of their surfaces was mirror-polished using mechanical and chemical polishing procedure. One of the sides of the (100) and (001) samples was parallel to [001] and [100] directions, respectively. The samples were prepared in the Institute of Electronic Materials Technology, Warsaw, and were kindaly supplied by Prof. A. Pajaczkowska.

Indentations were made on the (100) and (001) samples of SLA and SLG crystals using a PMT-3 microhardness tester fitted with a Vickers indenter with loads *P* between 5 and 100 g for 10 s. Two series of indentations were made on a sample. In the first series, the indentations was made in such a way that one of their diagonals was oriented along the longer edges of the samples, while in the second series one of the diagonals was oriented at an angle of 45^o relative to those of the first series on the same sample. Indentations were made on 3 samples of SLA(100), 2 samples of SLA(001), 2 samples of SLG(100) and 2 samples of SLG(001). The SLA and SLG samples of a given orientation in some cases differed in their colour, depending on the part of the cylindrical boule from where the sample were prepared.

On every sample, at a particular load at least 5 indentations with diagonals *d* parallel to the longer edges and 5 indentations with diagonals oriented by 45^o relative to the former ones were made. The dimensions of both diagonals of an indentation were measured, and the average dimension d was calculated from all diagonals made at a particular load *P*. For a particular indenter orientation the dimensions of different indentations produced on a sample at a given load did not differ from their average value by more than 1 %.

From the P(d) data the microhardness H_V was calculated using the standard relation:

$$H_V = kP / d^2, \tag{1}$$

where *k* is a geometric conversion factor for the indenter used. In the case of the Vickers indenter when *P* is taken in N and *d* is in μm, the geometrical conversion factor k = 1854 and H_V is in VHN (Vickers Hardness Number). However, when *P* is taken in N and *d* in μm, then the geometrical conversion factor is 0.1891 and hardness is in MPa, implying that 1 VHN = 9.8 MPa.

3. Experimental results and their analysis

It was observed that the hardness of both (100) and (001) planes of SLA and SLG samples exhibits reverse ISE, and the greatest influence of indenter orientation appears on the (100) plane. The anisotropy is more pronounced on SLA samples than on SLG samples. Fig. 1a-c illustrates typical examples of the reverse ISE on SLA and SLG samples. The figure shows plots of microhardness HV of three different samples against indentation diagonal *d*. Each of these figures presents the $H_V(d)$ data for orientation of indenter diagonal at angles 0^o and 45^o relative to the sample edge.

Examination of the indented surfaces of SLA and SLG samples revealed the appearance of cracks around indentations. Such cracks are typical for brittle materials.

In order to describe the ISE behaviour of materials, several relationships between the applied indentation test load *P* and indentation diagonal length *d* have been given in the literature (see refs. [3, 4]). The theoretical models describe the ISE phenomena through load-independent and load-dependent contributions represented by load-independent and load-dependent constants, respectively [3, 5-9]. The load-independent constants are used to calculate the material hardness. However, among the different ISE models, indentation-induced cracking model [10] and Meyer's law [5-8, 11] give load-independent constants with units different from conventional units of pressure. Therefore, they cannot be used to calculate load-independent hardness. The elastic/plastic deformation model proposed by Bull et al. [6] applies only to plastic materials where slip bands with a particular spacing between them are produced by indentation. Since SLA and SLG are brittle materials, this model is also not considered here.

For the analysis of the experimental indentation microhardness data on SLA and SLG samples Hays and Kendall's approach [9] and proportional specimen resistance model (PSR) [7, 8] are used below. Both these models have been proposed to explain normal ISE.

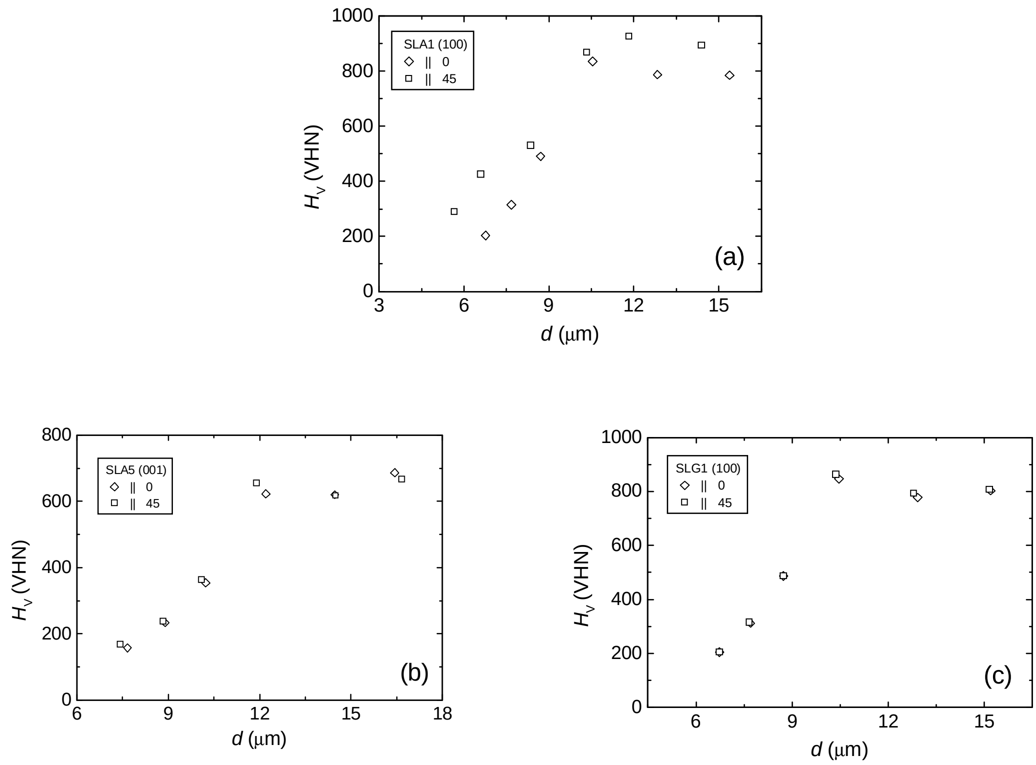

Fig. 1. Typical examples of the dependence of microhardness H_V on indentation diagonal d showing reverse ISE on different samples: (a) SLA1, (100) plane; (b) SLA5, (001) plane; and (c) SLG1, (100) plane. Orientation of indenter diagonal d at angles 0^o and 45^o relative to the sample edge is shown by diagonals and squares, respectively.

3.1. Hays and Kendall's approach

Hays and Kendall [9] proposed that the load dependence of hardness may be expressed by

$$P = W + A_1 d^2, \tag{2}$$

where W is the minimum load to initiate plastic (permanent) deformation and 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. Typical examples of the plots of P against d^2 are shown in Fig. 2, while the calculated values of W and A_1 for different samples are given in Table 1.

It may be seen from Table 1 that, irrespective of the chemical composition of the samples, the orientation of their planes and the indenter orientation, the values of W are negative. The values of W and A_1 depend on the chemical composition of the samples, the orientation of their planes and the indenter orientation. The maximum errors in the estimated values of W lie between 10 % and 38 %, while those in A_1 between 3 % and 11 %. The errors in W and A_1 are interrelated. For a sample the larger the error in the estimated W the larger is the error in the estimated A_1. These errors are directly reflected by the corresponding correlation coefficient (CC) for the best fit of the data.

It should be noted that, in general, the values of loads *W* to initiate deformation of the samples are about 15 g for the (100) plane and between 20 and 30 g for the (001) plane of the two crystals. It is difficult to find a rational explanation for such high values of *W*.

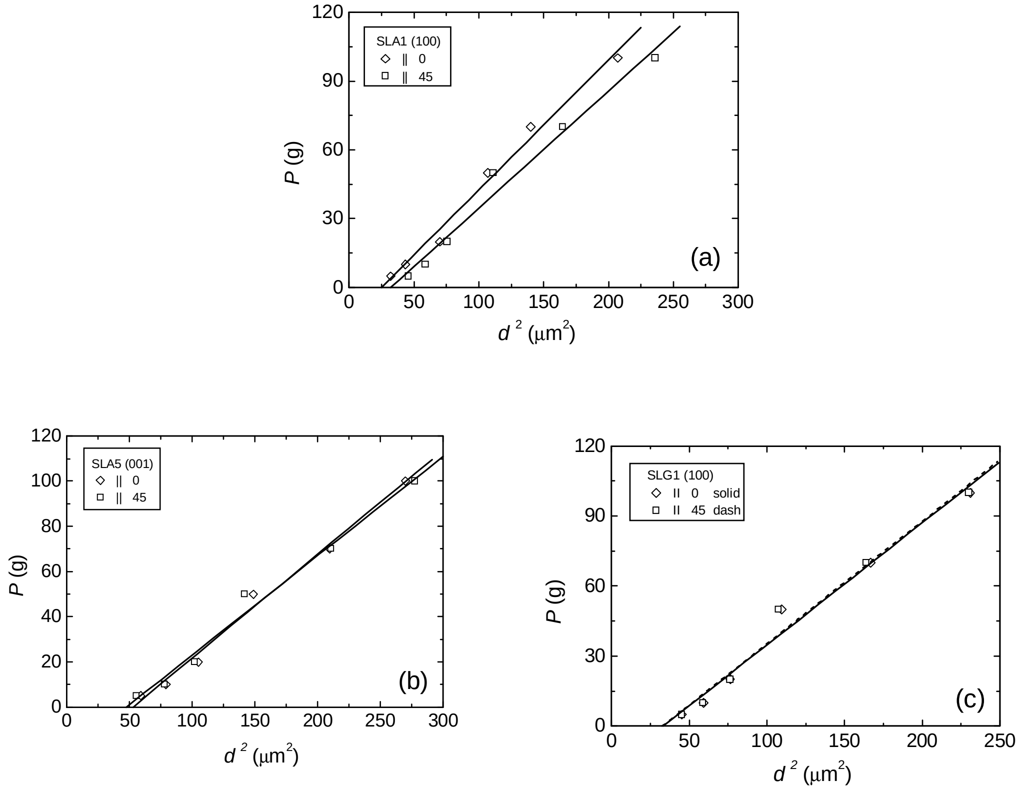

Fig. 2. Typical examples of the plots of *P* against d^2 for different samples: (a) SLA1, (100) plane; (b) SLA5, (001) plane; and (c) SLG1, (100) plane.

Table 1. Values of *W* and A_1 for different samples.

Sample	Plane	Indenter orientation					
		$d \parallel 0^o$			$d \parallel 45^o$		
		-*W* (g)	A_1 (g/µm^2)	CC	-*W* (g)	A_1 (g/µm^2)	CC
SLA1	(100)	16.38 ± 4.82	0.510 ± 0.036	> 0.990	14.10 ± 3.51	0.566 ± 0.030	> 0.994
SLA2	(100)	13.32 ± 3.74	0.559 ± 0.032	> 0.993	16.13 ± 1.59	0.595 ± 0.014	> 0.998
SLA3	(100)	15.81 ± 2.23	0.579 ± 0.019	> 0.997	14.95 ± 2.88	0.581 ± 0.025	> 0.996
SLA4	(001)	21.95 ± 3.52	0.440 ± 0.021	> 0.995	21.15 ± 3.98	0.430 ± 0.024	> 0.993
SLA5	(001)	24.30 ± 3.54	0.460 ± 0.022	> 0.995	20.72 ± 4.47	0.439 ± 0.027	> 0.992
SLG1	(100)	17.30 ± 4.77	0.521 ± 0.036	> 0.990	17.13 ± 5.12	0.525 ± 0.039	> 0.989
SLG2	(100)	14.95 ± 5.87	0.501 ± 0.044	> 0.984	13.46 ± 5.22	0.498 ± 0.040	> 0.987
SLG3	(001)	30.87 ± 6.78	0.462 ± 0.039	> 0.986	28.87 ± 7.60	0.451 ± 0.043	> 0.981
SLG4	(001)	30.21 ± 7.40	0.463 ± 0.043	> 0.983	29.07 ± 8.73	0.453 ± 0.050	> 0.976

3.2. Proportional specimen resistance (PSR) model

Several workers [7, 12-15] have proposed that the normal ISE behaviour may be described by the relation

$$P = ad + bd^2, \tag{3}$$

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 [14, 16], the deformed surface layer [17, 18], the indenter edges acting as plastic hinges [12], and the proportional specimen resistance [7, 8]. The constants a and b of Eq. (3) may be obtained from the plots of P/d against d for the samples. Typical examples of such plots are shown in Fig. 3, while the calculated values of a and b are listed in Table 2.

Table 2 shows that, irrespective of the chemical composition of the samples, the orientation of their planes and the indenter orientation, the values of a are negative. The values of a and b depend on the chemical composition of the samples, the orientation of their planes and the indenter orientation. The maximum errors in the estimated values of a lie between 5 % and 32 %, while those in b between 2 % and 16 %. As in the case of $W(A_1)$ data of Table 1, the errors in a and b are also interrelated. For a sample the larger the error in the estimated a the larger is the error in the estimated b. These errors are directly reflected by the corresponding correlation coefficient (CC) for the best fit of the $P(d)$ data.

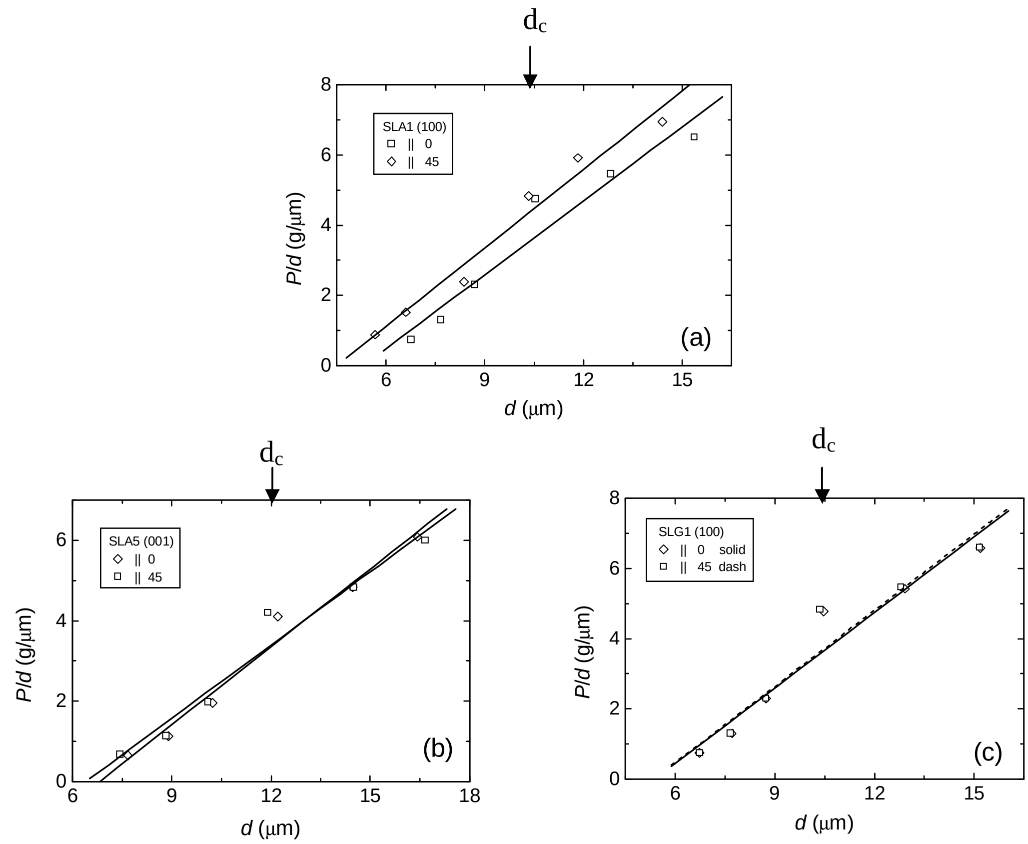

Fig. 3. Typical examples of plots of the P/d against d for different samples: (a) SLA1, (100) plane; (b) SLA5, (001) plane; and (c) SLG1, (100) plane. Orientation of indenter diagonal d at angles 0^o and 45^o relative to the sample edge is shown by diagonals and squares, respectively.

Table 2. Values of *a* and *b* for different samples.

Sample	Plane	Indenter orientation					
		$d \parallel 0^o$			$d \parallel 45^o$		
		-*a* (g/μm)	*b* (g/μm^2)	CC	-*a* (g/μm)	*b* (g/μm^2)	CC
SLA1	(100)	3.72 ± 0.95	0.701 ± 0.089	>0.969	3.35 ± 0.63	0.745 ± 0.063	> 0.985
SLA2	(100)	3.19 ± 0.65	0.729 ± 0.065	> 0.984	3.59 ± 0.15	0.776 ± 0.015	> 0.999
SLA3	(100)	3.59 ± 0.37	0.764 ± 0.037	> 0.995	3.30 ± 0.45	0.746 ± 0.045	> 0.992
SLA4	(001)	4.02 ± 0.59	0.618 ± 0.049	> 0.987	3.88 ± 0.66	0.595 ± 0.054	> 0.983
SLA5	(001)	4.40 ± 0.59	0.647 ± 0.049	> 0.988	3.89 ± 0.77	0.607 ± 0.064	> 0.978
SLG1	(100)	3.85 ± 0.96	0.716 ± 0.089	> 0.970	3.86 ± 0.72	0.722 ± 0.096	> 0.966
SLG2	(100)	3.49 ± 1.16	0.684 ± 0.108	> 0.953	3.15 ± 1.01	0.662 ± 0.094	> 0.961
SLG3	(001)	5.05 ± 0.80	0.657 ± 0.064	> 0.981	4.72 ± 0.89	0.633 ± 0.071	> 0.975
SLG4	(001)	4.95 ± 0.91	0.654 ± 0.072	> 0.976	4.81 ± 1.06	0.641 ± 0.084	> 0.967

4. Microhardness of SLA and SLG crystals

Tables 1 and 2 reveal that the correlation coefficient for the best fit of the *P*(*d*) data in PSR model is lower than that in the case of Hays-Kendall approach. A lower correlation coefficient for the best fit of the data in PSR model than in Hays-Kendall approach is associated with a transition in the plots of *P*/*d* against *d* (see Fig. 3) at a particular depth d_c, while no such transition is discerned in the plots of *P* against d^2 (see Fig. 2). The origin of these transitions will be discussed elsewhere [19].

As seen from Tables 1 and 2, the relative errors in the calculated values of *W* and *a* are comparable. Similarly, the errors in the calculated A_1 and *b* are comparable. Moreover, within the limits of the errors, the average values of *W*, A_1, *a* and *b* for the samples of a particular orientation of the indented plane are practically constant and do not depend on the origin of the sample. These values are given in Table 3.

Table 3. Average values of constants *W*, A_1, *a* and *b* for different samples.

Sample	Plane	Indenter orientation			
		$d \parallel 0^o$		$d \parallel 45^o$	
		-*W* (g)	A_1 (g/μm^2)	-*W* (g)	A_1 (g/μm^2)
SLA	(100)	15.17 ± 0.94	0.5494 ± 0.0203	15.06 ± 0.59	0.5808 ± 0.0084
	(001)	23.13 ± 1.17	0.4500 ± 0.0102	20.94 ± 0.21	0.4342 ± 0.0044
SLG	(100)	16.12 ± 1.18	0.5115 ± 0.010	15.29 ± 1.83	0.5114 ± 0.0134
	(001)	30.54 ± 0.33	0.4623 ± 0.0006	28.97 ± 0.10	0.4518 ± 0.0010
		-*a* (g/μm)	*b* (g/μm^2)	-*a* (g/μm)	*b* (g/μm^2)
SLA	(100)	3.50 ± 0.16	0.7312 ± 0.0181	3.42 ± 0.09	0.7559 ± 0.0103
	(001)	4.21 ± 0.19	0.6284 ± 0.0176	3.887 ± 0.003	0.6008 ± 0.0061
SLG	(100)	3.67 ± 0.18	0.7001 ± 0.0162	3.51 ± 0.35	0.6925 ± 0.0300
	(001)	5.00 ± 0.05	0.6553 ± 0.0013	4.77 ± 0.04	0.6366 ± 0.0039

Table 3 shows that the values of *W*, A_1, *a* and *b* for the samples of a particular orientation of the indented plane depend on the orientation of the indenter on the plane. However, this dependence is relatively poor and lies in the error limits. Thus, it may be concluded that the values of load-dependent constants *W* and *a*, and load-independent constants A_1 and *b* of SLA and SLG crystals depend mainly on the orientation of the indented plane. The values of the plane orientation-dependent microhardness of SLA and SLG crystals, calculated by multiplying the constants A_1 and *b* by the geometrical conversion factor 1854 for Vickers indenter, are listed in Table 4. The arithmetic mean values of A_1 and b for the two indenter orientations were used to calculate the microhardness.

Table 4. Average values of hardness (VHN) of SLA and SLG crystals.

Sample	Plane	Hardness (VHN)		
		HK*	PSR*	Refs. [1, 2]
SLA	(100)	1048	1378	648
	(001)	820	1140	358
SLG	(100)	948	1290	726
	(001)	848	1198	754

* Present work.

From Table 4 it may be concluded that SLA crystal is harder than SLG crystal and the (100) plane of both SLA and SLG is harder than their (001) plane. The difference in the microhardness of a particular plane of SLA and SLG crystals is associated with the difference in their cohesion energy and melting point (cf. ref. [1]), while the anisotropy in the hardness of the (100) and (001) planes of the crystals is a consequence of difference in the strength of Periodic Bond Chains lying in the planes (cf. refs. [20, 21]).

The values of microhardness, obtained in the present work, differ from those reported by Pajaczkowska and Gloubokov [1, 2], who found that SLG is harder than SLA crystals. Moreover, their data do not show the hardness anisotropy, as observed in the present study. Their hardness values are also lower than those obtained here, the difference being very large in the case of SLA crystals. This differences are indeed expected because the above authors determined hardness at constant loads of 50 and 100 g [22], where the effect of the indentation load is still present.

Note added in proofs by the editors:

For a comprehensive review of the developments in the field of indentation deformation of single crystals at loads ranging from several hundreds mN to a couple of μN, see [23].

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