Electronic Supplementary Material (ESI) for CrystEngComm. This journal is © The Royal Society of Chemistry 2020

Supporting information

# Crystal Structures and Electronic Properties of Sn<sub>3</sub>N<sub>4</sub> Polymorphs Synthesized *via* High-Pressure Nitridation of Tin

Ken NIWA<sup>1</sup>, Tomoya INAGAKI<sup>1</sup>, Tetsu OHSUNA<sup>1</sup>, Zheng LIU<sup>2</sup>, Takuya SASAKI<sup>1</sup>, Nico Alexander GAIDA<sup>1</sup>, Masashi HASEGAWA<sup>1</sup>

> <sup>1</sup>Department of Materials Physics Nagoya University Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

<sup>2</sup>National Institute of Advanced Industrial Science and Technology 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya, Aichi 463-8560 Japan

> Corresponding author: Dr. Ken NIWA Department of Materials Physics Nagoya University Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan TEL: +81-52-789-5515 FAX: +81-52-789-3252 E-mail: niwa@mp.pse.nagoya-u.ac.jp

## Additional Information for Experimental Details

#### Set-up for diamond-anvil cell and Laser heating

The diamond-anvil cell with the culet size of 350  $\mu$ m was used for all high-pressure experiments in this study (purchased from SYNTEK CO., LTD). The stainless steel (SUS) gasket with the initial thickness of 280  $\mu$ m was indented to the thickness of 20-30  $\mu$ m. The Q-switched pulsed cutting laser (DiNY pQ, IB Laser) with the wavelength of 1064 nm, 8 ns pulse width, 5~10 mJ/pulse, and maximum repetition frequency of 1 KHz was used for the fabrication of the sample hole. The pulsed laser beam with the diameter of 5-10  $\mu$ m was finely focused and it was irradiated to the surface of intended gasket which is turning around during the irradiation of the pulsed-laser beam. The laser heating for the compressed tin in molecular nitrogen was conducted by using CW-mode infrared laser (R3 series, SPI Laser) with the wavelength of 1090 nm and maximum power of 100 W. Both single-and double-sides laser heating is available in our laser heating system and the heating style can be changed depending on the sample conditions. The infrared laser was focused with the diameter of < 30  $\mu$ m at the sample position through the objective lens. A brief overview of the laser heating for each run is described later.

### Characterization of the synthesized products

The Raman and XRD measurements were conducted to characterize the synthesized samples. For Raman scattering measurements, argon ion laser with the wavelength of 488 nm (TEM00 mode, <50 mW, Beam diameter:0.65 mm (1/e<sup>2</sup>), divergence<30 mrad) was focused with the diameter of 5 -10  $\mu$ m through the objective lens (Mitsutoyo M PLAN) having 95 mm focusing distance, and it was irradiated to the sample through the diamond. The Raman scattered lights were dispersed with spectrometer (Princeton Instruments LP-2500, 500 mm focal length, 1800 grating/mm) and detected with liquid nitrogen cooled charge coupled device (Princeton Instruments PIXIS100B /ex). The single spectrum was measured with the exposure time of 5 sec and 20 spectra were totally accumulated to improve the noise to signal ratio. The whole sample was heated by slowly scanning the infrared laser and the quality of synthesized products was checked carefully at several different positions. If the quality of synthesized products was insufficient, the sample was heated again. In case of investigating the pressure dependence of Raman spectra, the spectrum was measured in the sample position as precisely as possible.

The synchrotron X-ray diffraction measurements were conducted at the high-pressure beam lines of Aichi Synchrotron Radiation Center (Aichi SR) and Photon Factory-Advanced Ring (PF-AR), KEK, as described in the main text. The name of beam line, X-ray size, X-ray detector are as follows, Aichi SR : BL2S1, 75 μm, ADSC Q315, PF-AR : NE1, 30 μm, Imaging Plate. The typical exposure time at BL2S1 and NE1 are 300 sec and 20 min, respectively. The whole area of the sample was heated

carefully, and the synthesis of tin nitrides were checked by Raman scattering measurements prior to the X-ray measurements. In order to observe the diffraction peaks at higher 2 theta angle under high pressure in the experiments at Aichi SR, the diffraction patterns were measured by tilting the diamond-anvil cell with approximate 17 degrees from the axis of the incident X-ray path. The X-ray size is almost comparable to or less than the sample size, and the diffraction patterns were measured from the almost center of the sample.

# Additional Information for Experimental Details

Run No.	P/GPa_bh	P/GPa_ah	Purpose of runs, and history of heating, compression, and decompression process			
Run1	16.2	16.2	For the synthesis of spinel phase:			
			Tin was heated in N <sub>2</sub> at 16.2 GPa with the laser power of 5 W for totally 30 min; However no Raman signal of the spinel			
			phase was observed, and the sample was further heated with the laser power of 20 W for 30 min. Then, the Raman			
			spectra were measured along with the decompression as shown in SI_#5.			
Run3	15.98-26.62	15.72-28.69	For the investigation of phase stability of synthesized products by high-pressure in-situ Raman spectroscopy:			
			Tin was heated in N <sub>2</sub> at approximately 15.98 GPa with the laser power of 5 -8 W for 30 min and the spinel phase was			
			confirmed by the Raman spectroscopy. Then, the sample was heated by an infrared laser after increasing the pressure of			
			a few GPa and evaluated by Raman spectroscopy. If the sample remained the spinel phase, it was compressed with more			
			a few GPa and heated again. The sample was evaluated by the Raman spectroscopy. These increscent of the pressure,			
			heating, and evaluation, were conducted up to 28.69 GPa. Then, the sample was further compressed and heated as in the			
			lower pressure process up to 36.84 GPa. However, the Raman spectrum remained the same. Next, the pressure was			
			continuously decreased within a few GPa steps, while the Raman spectrum was measured at each step. After the Raman			
			spectrum was changed at around 22.3 GPa, we increased the pressure again to 34.9 GPa. After that, the pressure was			
			decreased again while the sample was monitored by Raman spectroscopy, until the spectrum drastically changed at 9.7			
			GPa. Then, the sample was compressed again up to 17.4 GPa from 9.7 GPa and after reconfirmation of the new profile,			
			the sample was finally recovered into ambient pressure. These decompression and re-compression cycles were			
			conducted under room temperature (no laser heating). The measured spectra are shown in SI_#4.			
Run11	37.5	36.0	For the investigation of the stability of monoclinic $Sn_3N_4$ by high-pressure in-situ XRD measurements:	Fig.4, SI_#6,		
			Tin was heated in $N_2$ at approximately 15 GPa to synthesize the spinel phase. Then, the pressure was increased to 37.5	SI_#15		
			GPa and it was laser-heated with the laser power of 10 W for 10 min. The synthesis of monoclinic phase was confirmed			
			by the high-pressure in-situ XRD measurements at BL2S1 and the XRD profiles were measured along with the			
			decompression into ambient pressure. The data set were plotted in the compression curve of Fig.4.			
Run15	36.3	35.8	For the checking of reproducibility of the high-pressure phase and its transition along the decompression:	Fig.4, SI_#15		

			Tin was heated in $N_2$ at 36.3 GPa with the laser power of 15 W for 10 min to directly synthesize the monoclinic phase.		
			The XRD profiles were measured along with the decompression into ambient pressure. The data set were plotted in the		
			compression curve of Fig.4.		
Run22	34.1	32.4	4 For the checking of reproducibility and SEM observation:		
			Tin was heated in N <sub>2</sub> at 34.1 GPa with the laser power of 15 W for 10 min to directly synthesize the monoclinic phase.		
			The synthesis of monoclinic phase was confirmed by Raman spectroscopy as shown in SI_#1. The ambient recovered		
			sample was analyzed by SEM-EDX.		
Run34	19.2	19.9	For the synthesis of spinel phase and TEM observation:		
			Tin was heated in N <sub>2</sub> at 19.2 GPa with the laser power of 20 W for 20 min to directly synthesize the spinel phase. The		
			sample was carefully monitored by using an optical microscope to check the change of absorption properties for visible		
			light. The sample appearance was changed as follows; almost transparent (20 GPa) => translucent yellow (10 GPa) =>		
			translucent orange (0.1 MPa). The ambient recovered sample was characterized by TEM (not shown here).		
Run39	23.2	22.3	For the morphology observation of the spinel phase by SEM:	SI_#8, #9	
			Tin was heated in N <sub>2</sub> at 23.2 GPa with the laser power of 15 W for 10 min to directly synthesize the spinel phase. The		
			sample was recovered into ambient pressure and the morphology and chemical composition were analyzed.		
Run40	33.4	32.9	For the morphology observation of the ambient recovered orthorhombic phase by SEM:	SI_#8, #9	
			Tin was heated in N <sub>2</sub> at 33.4 GPa with the laser power of 10 W for 20 min to directly synthesize the monoclinic phase.		
			The sample was recovered as the orthorhombic phase into ambient pressure and the morphology and chemical		
			composition were analyzed as well as spinel phase.		
Run45	145     34.0     34.4     For the structural refinement of the ambient recovered orthorhombic phase:		For the structural refinement of the ambient recovered orthorhombic phase:	Fig.3(e),	
			The synthesis of the new phase was confirmed based on the several experimental runs while the high-quality data are	Fig.4,	
			required to reveal the details of crystal structure especially for the ambient recovered phase. Three independent synthesis	SI_#10-15	
Run47	33.0	34.0	experiments (Run 45, 46 and 47) were conducted based on the similar conditions as follows, tin was heated in $N_2$ at 33	Fig.1(a)-(c)	
			- 34 GPa with the laser power of 15 W for 30 min. The synthesis of the monoclinic phase was confirmed by Raman		
			spectroscopy in all runs. The synthesized samples were recovered into ambient pressure and the quality was preliminary		
			assessed with an in-house instrument using the Debye-Scherrer diffraction geometry and Cu-Ka radiation. As the results,		

			it was found that the sample of Run 45 was of better quality in comparison with the other samples, although the remnants			
			of starting material (tin) were detected. The XRD profile of the sample of Run45 was measured in BL2S1 with the			
			exposure time of 240 sec and the results of refinements are shown in Fig.3(e), Fig.4 and SI_#10-15.			
Run48	53.9	52.2	For the investigation of the phase stability of the monoclinic phase by high-pressure in-situ XRD measurements:	Fig.4, SI_#15		
			Tin was heated in N <sub>2</sub> at 53.9 GPa with the laser power of 20 W for 10 min to directly synthesize the monoclinic phase.			
			The XRD profiles were measured along with the decompression. The data set were plotted in the compression curve of			
			Fig.4.			
Run54	32.4	31.9	For the investigation of the phase stability of the monoclinic phase by high-pressure in-situ XRD measurements:	Fig.4, SI_#15		
			Tin was heated in N <sub>2</sub> at 32.4 GPa with the laser power of 10 W for 10 min to directly synthesize the monoclinic phase.			
			The XRD profiles were measured along with the decompression. The data set were plotted in the compression curve of			
			Fig.4.			
Run56	38.4	36.5	For the investigation of the phase stability of the monoclinic phase by high-pressure in-situ XRD measurements:	SI_#7		
			Tin was heated in $N_2$ at 38.4 GPa with the laser power of 10 W for 10 min to directly synthesize the monoclinic phase.			
			The XRD profiles were measured at NE1, PF-AR. The obtained data were almost consistent with those measured at			
			Aichi SR while the profile at 17 GPa which is corresponding to the condition for the intermediate phase, is of somewhat			
			better quality.			
Run58	34.4	38.2	For the investigation of the phase stability of the monoclinic phase by high-pressure in-situ XRD measurements:	Fig.2, Fig.4,		
			Tin was heated in $N_2$ at 34.4 GPa with the laser power of 10 W for 10 min to directly synthesize the monoclinic phase.	SI_#15		
			The XRD profile was used for the Le Bail analysis and charge flipping method. The XRD profiles were measured along			
			with the decompression and the data set were plotted in the compression curve of Fig.4.			
SnN_III	44.6	45.5	For the characterization of the ambient recovered orthorhombic phase:	Fig.3(a)-(d)		
			Tin was heated in $N_2$ at 34.4 GPa with the laser power of 15 W for 10 min to directly synthesize the monoclinic phase.			
			The XRD profiles were measured after heating and along with the decompression at the NE1, PF-AR. Although the tin			
			remained after laser heating, the intense diffraction peaks of the monoclinic phase were observed. The ambient recovered			
			sample was analyzed by TEM-EDS for further detailed characterization.			

"bh" and "ah" represent the "before heating" and "after heating", respectively.



 $SI_{41}$  Raman spectra measured at before heating at 34.1 GPa and after heating at 32.4 GPa Several unlabeled peaks which were appeared after laser heating, correspond to the monoclinic  $Sn_3N_4$ . The Raman spectra of spinel-type  $Sn_3N_4$  and pyrite-type  $SnN_2$  are also shown for comparison.

	U	÷ .	
hkl	$d_{\rm obs.}$ (Å)	$d_{\text{cal.}}$ (Å)	$d_{\mathrm{obs.}}$ - $d_{\mathrm{cal.}}$ (Å)
020	4.9101	4.9137	-0.0036
110	4.4585	4.4709	-0.0124
120	3.5062	3.5116	-0.0054
10-1	2.8763	2.8763	0.0000
011	2.8067	2.8077	-0.0010
130	2.7473	2.7434	0.0039
200	2.5110	2.5102	0.0008
12-1	2.4823	2.4823	0.0000
111	2.2278	2.2259	0.0019
140	2.2065	2.2067	-0.0002
031	2.1827	2.1838	-0.0011
14-1	1.8686	1.8681	0.0005
150	1.8306	1.8302	0.0004
15-1	1.6236	1.6227	0.0009

SI\_#2-1 Peak indexing of monoclinic Sn<sub>3</sub>N<sub>4</sub> at 33 GPa

a = 5.1988(46) Å, b = 9.8273(53) Å, c = 3.0339(19) Å,  $\beta = 105.05(7)^{\circ}$ 

The lattice parameters were refined by least-squares against the peak positions of the reflections using DICVOL6 software.



SI\_#2-2 Peak indexing of monoclinic Sn<sub>3</sub>N<sub>4</sub> at 33 GPa

The 2 theta positions marked with asterisk are used for indexing. The red vertical lines represent the peak positions of  $P2_1/n$  space group. The residual peaks are also assigned with the obtained unit cell.



SI #2-3 XRD profiles of laser heated tin in molecular nitrogen at 33 GPa

Unrolled 2-D image shows the spots which are derived from both synthesized tin nitrides and molecular nitrogen. The vertical axis of the unrolled 2-D image represents the azimuth angle. The 1-D XRD pattern is superimposed on the 2-D unrolled image and "Intensity (arb. units)" corresponds to the vertical axis. These demonstrate that highly crystalline tin nitrides are likely to be grown at high temperature by laser heating under high pressure. Due to the strong spots in the Debye-Scherrer rings resulting from relatively large sample crystallites and limitation of 2 theta angles, the structural refinement by Rietveld method was not possible, hence the peak indexing and Le Bail analyses were performed. In addition, the position of Sn and N were preliminary obtained by the charge flipping method based on the extracted intensity data from Le Bail analysis. The intensity data yield no significant change if the 1-D conversion was conducted after eliminating the intense spots. Thus, the present converted profile likely reflects the reasonable intensity ratios due to the averaged distribution of the grain. However, in order to further characterize the structure by full structural analysis such as Rietveld refinement, the diffraction profile should be improved by rotating the DAC and using short wavelength.

Formula	$\mathrm{Sn_3N_4}$	
Crystal system, space group	monoclinic, $P2_1/n$ (No.14)	
Cell parameters	a = 5.1849(5) Å	
	b = 9.8396(8) Å	
	c = 3.0304(2) Å	
	$\beta = 105.344(6)^{\circ}$	
Final <i>R</i> -factors		
$R_{_{ m wp}}$	2.235 %	
R <sub>p</sub>	1.165 %	
$R_{ m B}$	1.874 %	
S	1.322	

SI\_#3-1 Refinement results of Le Bail analysis for monoclinic Sn<sub>3</sub>N<sub>4</sub> at 33 GPa

SI\_#3-2 Sn and N positions obtained by direct space method based on the results of Le Bail analysis

Atom	x	у	Ζ
Sn (1)	0.5	1.0	1.0
Sn (2)	0.0267	0.1537	0.2541
N (1)	0.6986	0.8410	0.0100
N (2)	0.2344	0.9383	0.3102

a = 5.1849(5) Å, b = 9.8396(8) Å, c = 3.0304(2) Å,  $\beta = 105.344(6)^{\circ}$ 



SI\_#4 Raman spectra measured under high pressures at room temperature

(a) The intense peaks at 36.8 GPa correspond to the monoclinic Sn<sub>3</sub>N<sub>4</sub>. Along with the decompression, new peaks marked by the arrows were starting to grow at 24.9 GPa and more clearly seen at 22.3 GPa. These new peaks were disappeared when the sample was compressed again up to 34.9 GPa and the profile at this pressure is like that at 36.8 GPa. (b) The sample was decompressed slowly again from 34.9 GPa and the profile was changed to be same as observed at approximately 25 GPa. Further decompression yielded the drastic reduction of the intensity and the appearance of very weak peaks (dashed arrows) at approximately 9.7 GPa. Then, the sample was compressed again from 9.7 GPa to 17.4 GPa and same Raman profile was appeared again. Very weak intense peaks were observed again after the decompression to the ambient pressure from 17.4 GPa. It was found from the Raman scattering experiments that the spectra are reversible changed with pressure.



SI\_#5 The pressure dependences of Raman peak frequencies measured along decompressing process The solid symbols represent the Raman peak frequencies derived from the  $Sn_3N_4$  polymorphs. The pressure dependences of Raman peak frequencies for  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub> is also shown with open circles and solid lines.



SI\_#6 Synchrotron PXRD patterns measured along to the ambient pressure from 36.5 GPa under room temperature

(a) The diffraction peaks marked by arrows correspond to solid  $N_2$ , and the other peaks are derived from the high-pressure synthesized tin nitrides. (b) The enlarged patterns at the lower  $2\theta$  region are also shown to facilitate the change of the profiles. The solid triangles, open circles, and solid circles correspond to the ambient recovered orthorhombic phase, high-pressure intermediate phase which is appeared between 10 and 25 GPa, and monoclinic phase, respectively.



SI\_#7 Peak indexing of intermediate high-pressure phase Sn<sub>3</sub>N<sub>4</sub> at 17 GPa

The two theta positions marked with asterisk are used for indexing. The obtained lattice parameters are a = 10.188(3) Å, b = 10.041(2) Å, and c = 3.136(1) Å (V= 320.88 Å<sup>3</sup>). The red vertical lines represent the peak positions of *Pbnm* space group and the residual peaks are also assigned with the obtained unit cell. The expected space group of *Pbnm* and the lattice parameters (and unit cell volume) are very similar to the ambient recovered orthorhombic ones. This indicate that the number of Sn<sub>3</sub>N<sub>4</sub> in the unit cell is same as that of ambient pressure phase (Z=4), although the extrapolated lattice parameters show the discontinuity changes at approximately 10 GPa.



SI\_#8 SEM images of (a)  $\gamma\text{-}Sn_3N_4$  and (b) new  $Sn_3N_4$  polymorph



SI\_#9 EDS spectra of  $\gamma\text{-}Sn_3N_4$  and new tin nitride

The N/Sn are averaged values based on the several point analyses. The Pt-M $\alpha$  and Cu-L $\alpha$  peaks in the spectra are due to the attachment of a sputtering target in order to avoid the electron charge-up of the sample. The C-K $\alpha$  and O-K $\alpha$  peaks might be derived from the carbon tape which is used to fix the sample.



SI\_#10 Measured XRD profile at 0.1 MPa together with simulated profile of  $\beta$ -Sn^1),  $\gamma$ -Sn\_3N\_4^2), and SnN\_2^{3)}

1) Wyckoff, R. W. G., Crystal Structures, 1963, 1, 7-83, Second edition. Interscience Publishers, New York

2) N. Scotti, W. Kockelmann, J. Senker, Z. Anorg. Allg. Chem. 624 (1999) 1435-1439

3) K. Niwa, H. Ogasawara, M. Hasegawa, Dalton Transactions 46 (2017), 9750-9754





The unrolled 2-D image is shown together with 1-D conventional profile having the vertical axis of "Intensity (arb. units)". The azimuth angle corresponds to the vertical axis of 2-D image. The XRD profile was measured during the 360° rotation around  $\omega$ -axis. The spotted lines are derived from residual tin. The Debye ring shows smoothly but slightly the variation of intensity in the same *hkl* lines probably due to the lattice preferred orientation.

hkl	$d_{\rm obs.}$ (Å)	$d_{\mathrm{cal.}}(\mathrm{\AA})$	$d_{\rm obs.}$ - $d_{\rm cal.}$ (Å)
200	5.43759	5.4369	0.00069
020	5.07713	5.07409	0.00304
210	4.79333	4.79244	0.00088
220	3.70981	3.70956	0.00025
111	3.09645	3.09768	-0.00123
320	2.94963	2.94939	0.00024
021	2.82834	2.8297	-0.00137
121	2.74244	2.7385	0.00394
410	2.62431	2.62587	-0.00156
040	2.53868	2.53704	0.00164
301	2.48043	2.48327	-0.00284
420	2.39651	2.39622	0.00029
141	1.99964	2.00054	-0.00089
331		2.00178	-0.00214
520		1.9989	0.00074
241	1.9063	1.9061	0.0002
600	1.81192	1.8123	-0.00039
341	1.775	1.77464	0.00035
002	1.70331	1.70452	-0.00121
202	1.62742	1.62646	0.00096
450		1.62635	0.00107
022	1.61674	1.61579	0.00095
260		1.61502	0.00172
360	1.53158	1.5327	-0.00112
621	1.52723	1.52613	0.0011
161	1.50064	1.50064	0.00001
322	1.47513	1.47579	-0.00066
640		1.47469	0.00044
322	1.47513	1.47579	-0.00066
640		1.47469	0.00044

SI\_#12-1 Peak indexing of orthorhombic  $Sn_3N_4$  at ambient pressure

a = 10.873(3) Å, b = 10.148(3) Å, c = 3.409(1) Å

\_

The lattice parameters were refined by least-squares against the peak positions of the reflections using DICVOL6 software.



SI\_#12-2 Peak indexing of orthorhombic Sn<sub>3</sub>N<sub>4</sub> at ambient pressure

The two theta positions marked with asterisk are used for indexing. The red vertical lines represent the peak positions of *Pbnm* space group. Although Sn remains in this sample, almost all peaks are assigned with the obtained unit cell.



SI\_#13 XRD profile of newly synthesized Sn<sub>3</sub>N<sub>4</sub> with different synthetic process

The upper profile corresponds to the XRD profile of the sample which was obtained from the compression experiment of  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub> up to 48 GPa with no laser heating and recovery into ambient pressure. The lower blue line profile corresponds to the sample which was obtained from the direct nitridation experiment (Fig.3(e)). Tips correspond to the Bragg peak positions of  $\gamma$ -Sn<sub>3</sub>N<sub>4</sub> (upper) and  $\beta$ -Sn (lower), respectively.





The XRD profile with  $CaFe_2O_4$ -type structure is simulated based on the experimentally determined lattice parameters and the cationic positions (Ca and Fe) of  $CaFe_2O_4$ . The nitrogen positions were not taken into account for the simulation.



SI\_#15 (a) The crystal structure of  $BeY_2O_4$ . The green triangles indicate the  $BeO_3$  plane, and their vertices are shared with the YO<sub>6</sub> octahedra. The YO<sub>6</sub> polyhedra are connected by edges sharing. (b) Sn arrangement of the new tin nitride obtained from the refinement of the XRD profile based on the  $BeY_2O_4$  as the model structure. (c) The crystal structure of the new tin nitride viewed from the *c*-axis after optimization by using CASTEP program. The fivefold and sixfold coordinated polyhedra are shown with dark green and blue colors, respectively. (d) The 301 plane which is mainly composed of N atoms. (e) The measured data around the 301 peak are plotted with red cross for the sample of Run 45. The simulated profiles with the case of fully occupied and unoccupied nitrogen are also shown with solid green and blue lines, respectively. The residuals between the data and simulated profiles are shown with the dashed lines.



SI\_#16 Pressure dependence of the lattice parameters for monoclinic and orthorhombic phases The *a*-axis of monoclinic phase is shown by the multiple of the original unit cell constant. The axial lengths between monoclinic and orthorhombic phases indicate that the monoclinic phase crystallographically relates to that of orthorhombic phase. The anisotropic axial compression was observed as the following axial compressibility ;  $\beta_{c, 0\text{GPa}} (1.02 \times 10^{-3} \text{ GPa}^{-1}) > \beta_{b, 0\text{GPa}} (0.97 \times 10^{-3} \text{ GPa}^{-1})$  $\beta_{a, 0\text{GPa}} (0.80 \times 10^{-3} \text{ GPa}^{-1})$  and  $\beta_{c, 25\text{GPa}} (2.20 \times 10^{-3} \text{ GPa}^{-1}) > \beta_{a, 25\text{GPa}} (1.97 \times 10^{-3} \text{ GPa}^{-1}) > \beta_{b, 25\text{GPa}} (1.02 \times 10^{-3} \text{ GPa}^{-1})$  for monoclinic and orthorhombic phases, respectively.