Negative Area Compressibility in Silver Oxalate

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Abstract. The presence of extremely large negative linear compressibilities (NLC) in crystalline silver oxalate was discovered in a recent work by using first principles solid-state calculations. Although the minimum value of the NLC was found for a negative applied hydrostatic pressure, in this work the presence of NLC in this material for positive applied pressures is verified experimentally by means of high pressure X-ray diffraction experiments performed at room temperature in the Beijing Synchrotron Radiation Facility (BSRF). The results of this study demonstrate with certainty that the compressibility of silver oxalate along [010] crystallographic direction is negative for applied pressures in the range from 0.0 to 0.85 GPa. Since the measured compressibility decreases largely as the pressure decreases, large negative values of the compressibility are expected for negative applied pressures in agreement with the results found using first principles methods. Furthermore, the analysis of the variation of the lattice parameters of the crystal structure of silver oxalate under pressure in the principal axes reference system, revealed that this material also exhibits the largest negative area compressibility phenomenon found so far at zero pressure, the values of the compressibilities along two of the principal axes being -16.7 and -20.0 TPa⁻¹. The negative compressibility phenomenon in silver oxalate can be rationalized in terms of a “chains of rotating parallelograms” structural model.

Introduction

In a recent paper [1], the presence of large negative linear compressibilities (NLC) [2–12] in crystalline silver oxalate, Ag₂C₂O₄, was discovered by using high quality first principles solid-state calculations based in Density Functional Theory employing large plane wave basis sets and pseudopotential functions [13–14]. In fact, the absolute value of minimum compressibility found for silver oxalate, -831.9 ± 10 TPa⁻¹, is the largest found so far and the range of applied hydrostatic pressures for which this compound

exhibits NLC is also the widest found up to date [1]. The crystal structure of silver oxalate, its mechanical properties and the deformation of the crystal structure under pressure at the basis of the NLC phenomenon in this material were described in detail [1]. NLC effects were also found for oxalic acid [15–16] and other oxalate materials as ammonium oxalate monohydrate [17] and the anhydrous zinc and cadmium oxalates [18].

Although a wide range of important potential applications [2–3,10,12,19–21] for NLC materials have been found, the NLC phenomenon is quite infrequent [10] and the magnitude of the negative compressibility and the range of applied pressures for which these materials show NLC is frequently too small to be exploited in practical applications. The NLC effect found for silver oxalate [1] is very relevant not only due to its inherent significance. Since the differences in the magnitude of the minimum compressibility and NLC pressure range with respect to previous findings are very large, they indicate that the possibility of discovering even larger NLC effects is indeed significant. Silver oxalate is a compound which is used in photographic emulsions [22] and in a large series of technological applications [23–36] including the development of films for screen, electro-photographic and ink-jet printing [25–26]. In nanotechnology [23–34,26–28] it is widely used because the controlled thermal [38–31] or mechanical [32–35] decomposition of silver oxalate produces metallic nanoparticles with technologically desirable properties. In particular, silver nanoparticles have antimicrobial properties and are incorporated during the synthesis of compounds used as dental composites and in artificial bone materials [24,36]. Several easy high-yielding synthetic procedures [23,26,28,37–38] are known and, therefore, silver oxalate is a compound with large availability. The simplicity and availability of this compound suggest that the search of NLC materials should cover also common materials [12,15–16,18,39]. The presence of silver in several well-known NLC materials [40–43] is noteworthy.

While the results from high-quality first principles computations are generally in good agreement with experimental data, the predictions arising from this type of theoretical calculations may diverge from the expectations due to a large number of factors. One of the most important factors is the temperature because the first principles calculations correspond to zero temperature and the most interesting applications require that the NLC effect be observed at room temperature. Therefore, the predictions should always be corroborated by experimental measurements performed at interesting conditions. For this

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reason, an experimental high-pressure X-ray diffraction study of the negative linear compressibility effect in silver oxalate was carried out at the Beijing Synchrotron Radiation Facility (BSRF) [44].

Materials and methods

The experiments were performed with a crystalline powder sample of silver oxalate (CAS number 533-51-7, 99.02% purity) provided by Shanghai Ichemical Co., Ltd. The compound was rigorously identified from X-ray diffraction experiments (see the next Section). The sample was used as received without further purification in the high pressure X-ray diffraction experimental study.

The high-pressure X-ray diffraction experiments were performed at the 4W2 beam line of Beijing Synchrotron Radiation Facility [44]. The X-ray beam at the wavelength 0.6199 Å was focused into a $36 \times 12 \mu\text{m}^2$ spot using Kirkpatrick–Baez mirrors. The hydrostatic pressure was exerted by the systematic diamond anvil cells (DAC) [45] with the culet diameter of 400 μm . The samples in well grinded powder were placed in a hole of about 120 μm diameter in a pre-indented stainless steel gasket with the thickness of 40 μm . Silicon oil was adopted to act as the pressure-transmitting medium and ruby chips were placed for pressure calibration by measuring the fluorescence shift as a function of pressure [46]. The diffraction patterns were

recorded by a Pilatus image plate and integrated with the FIT2D software package.

Results and discussion

The X-ray diffraction powder patterns of silver oxalate obtained at four different applied hydrostatic pressures (0.0, 0.134, 0.478 and 0.848 GPa) are shown in Fig. 1. The four patterns are provided as Supplementary Material. The reference X-ray powder pattern of silver oxalate was determined in our previous work [1] from the experimental unit cell reported by Naumov *et al.* [47] in 1995. The measured X-ray diffraction powder pattern at zero pressure is compared with the reference pattern in Fig. S.1 of the Supplementary Material. The precise values of the positions of the most important reflections in the powder pattern at 0.0 GPa and the corresponding data from the reference pattern are given in Table S.1. Both sets of data are in excellent agreement, the largest deviations being about 0.02 Å. These results confirm the good quality of the sample used in the present study. However, the presence of two extra peaks in the measured X-ray diffraction pattern at 15.12° and 17.47° must be noticed. These two peaks are due to the presence of an impurity of pure metallic silver without impact on the general crystallinity of the sample as shown in Fig. S.2 of the Supplementary Material.

Fig. 1. X-ray powder patterns of silver oxalate under pressure. The position of the [011], [100], [020] and [-1-11] reflections is indicated.

Four well-defined reflections in the X-ray powder pattern were selected to extract the lattice parameters of the crystal structure of silver oxalate. These reflections are [-1-11], [011], [020] and [100]. The expressions used to derive the lattice parameters from the positions of these reflections are

given in Appendix A. The values of the lattice parameters obtained at the four different pressures are reported in Table 1. Again, the lattice parameters obtained at zero pressure are in very good agreement with the reference data from Naumov *et al.* [47] (given also in Table 1), the values of the

b lattice parameter differing by less than 0.1%. As can be seen in Table 1, the lattice parameters obtained using first-principles calculations [1] are also in good agreement with the experimental results, the computed unit-cell volume differing from the experimental one by 1.1%. From the

computed crystal structure the mechanical properties of silver oxalate were determined theoretically [1]. A short survey of the results obtained, including the bulk modulus and its pressure derivatives as well as the computed elasticity matrix are given in Table S.2 of the Supplementary Material.

Table 1. Lattice parameters of silver oxalate under pressure. The parameters at zero pressure are compared with the parameters from the reference pattern from Naumov *et al.* [47] and those obtained in the first principles calculations [1].

Parameter	P = 0.0 GPa			P = 0.134 GPa	P = 0.474 GPa	P = 0.848 GPa
	Naumov <i>et al.</i> [47]	DFT [1]	Present work			
a (Å)	3.4603(5)	3.5713	3.4765	3.4608	3.4381	3.4138
b (Å)	6.1972(9)	6.0319	6.1932	6.2058	6.2184	6.2317
c (Å)	9.548(2)	9.4867	9.5796	9.5492	9.5323	9.3933
β (deg)	103.47(10)	105.5823	103.6911	103.3643	102.9055	100.9885
Vol. (Å ³)	199.12(6)	196.8535	200.3926	199.5341	198.6475	196.1681

As can be observed in Table 1, the b lattice parameter of silver oxalate increases invariably from 0.0 to 0.848 GPa. These results confirm with certainty the negative linear compressibility phenomenon in silver oxalate, in agreement with the results of the first principles calculations [1] at zero temperature. The phenomenon persists at room temperature. In order to determine the compressibility of silver oxalate at zero pressure from the structural data obtained in the high pressure experiments, the approach proposed by Cliffe and Goodwin [48] in 2012 was used. Thus, the PASCAL online tool [49] was employed. The values obtained for the linear compressibilities in the principal axes reference system are given in Table 2.

Table 2. Linear compressibilities of silver oxalate in the principal axes reference system.

Principal axis (u_i)	k_i (TPa ⁻¹)
$u_1 = [0.9791, 0.0, -0.2033]$	61.36
$u_2 = [0.0, 1.0, 0.0]$	-16.73
$u_3 = [0.8910, 0.0, 0.4540]$	-19.98

To test the values obtained using PASCAL software, a fit of the values of the b lattice parameter (as a function of the applied pressure) to a Birch-Murnaghan [50] equation of state (BM-EOS) was performed using Angel's EOSFIT 5.2 software [51–52]. From the fitted value of the bulk modulus, the compressibility along b direction, $k_b = -1/b \cdot (\partial b / \partial P)_P$, was obtained. Since the [010] crystallographic direction coincides with the second principal axis, the value obtained for k_b agreed very well with the value of k_2 given in Table 2. The final value for the compressibility along [010] direction, including the standard deviation obtained with EOSFIT code, is $k_2 = -16.7 \pm 0.2$ TPa⁻¹.

From the results given in Table 2, it follows that the linear compressibilities of silver oxalate along two directions of the principal axes are negative. Therefore, silver oxalate displays the negative area compressibility phenomenon [10,16,43,53–59] at zero pressure. The compressibility along the first principal axis is positive and very large to compensate for the negative values of the compressibilities

along the second and third axes. The linear compressibilities obtained for silver oxalate are compared in Table S.3 of the Supplementary material with a selection of values of the compressibilities for the most important NLC materials at zero pressure known so far. The absolute value of the negative compressibilities, k_2 or k_3 , is larger than those of most materials, except CsH₂PO₄ [60], Ag₃[Co(CN)₆] [41–42], Zn[Au(CN)₂]₂ [61], MIL-53 [62] and InH(BDC)₂ [63]. However, the absolute value of the compressibility of silver oxalate along b direction obtained from first principles calculations at $P = -0.16$ GPa is much larger than the compressibilities in these materials.

Since for silver oxalate the compressibilities along two directions are negative, the comparison with other systems exhibiting NAC is more appropriate. The value of the largest compressibility in three different NAC materials, NaV₂O₅ [53–55], TlGaSe₂ [56] and Ag[C(CN)₃] [43] are given in the last rows of Table S.3. As can be seen, the absolute values of the compressibilities in silver oxalate are much larger than those of these materials.

In order to compare the values of the compressibilities obtained in the first principles calculations with the experimental values at non-zero pressures, the values of the compressibility, $k_b = -1/b \cdot (\partial b / \partial P)_P$, were evaluated at selected pressures between 0.10 and 0.20 GPa from the BM-EOS. The results are given in Table 3. For example, at 0.13 GPa, the compressibility is $k_b = -11.7$ TPa⁻¹, which may be compared with the theoretical value of -21.3 TPa⁻¹. The agreement is reasonable in view of the fact that the theoretical result corresponds to zero temperature and the experimental one to room temperature and taking into account the approximate nature of the first principles calculations. The variation of the measured b lattice parameter and associated compressibility at small external pressures is displayed in Fig. 2. The absolute value of the compressibility increases drastically as the pressure decreases. Therefore, large negative compressibilities at negative pressures are expected in agreement with the results obtained in the first principles work [1].

Table 3. Comparison of the compressibilities of silver oxalate for a selected set of pressures in the range from 0.1 to 0.2 GPa with the values obtained from first principles calculations [1].

Pressure (GPa)	Exp. $k_b(\text{TPa}^{-1})$	DFT $k_b(\text{TPa}^{-1})$
0.11	-12.7	-27.5
0.13	-11.7	-21.3
0.15	-10.7	-18.5
0.17	-9.8	-18.0
0.19	-9.0	-19.0

Fig. 3. Experimental b lattice parameter and compressibilities of silver oxalate for small external pressures.

NLC mechanism in silver oxalate

The structural mechanism leading to the presence of NLC in silver oxalate, studied in the earlier paper [1], was reinvestigated in this work. Figs. 3.A and Fig. 3.B provide

views of the crystal structure of silver oxalate under the effect of two different increasing isotropic pressures -0.394 and -0.127 GPa) parallel to (yz) and (xz) planes. Under compression, the b lattice parameter increases strongly and the other two parameters decrease to compensate the increase of b so that the total unit-cell volume decreases. An inspection of the views of the crystal structure of silver oxalate, provided in Fig. 3, shows the presence of chains of parallelograms expanding along $[010]$ and $[100]$ direction connected by the oxalate groups. The parallelograms do not share an edge but a vertex (occupied by a silver atom) and are rotated relative to each other. These chains, isolated of the structure, are displayed in Fig. 3. As is well-known [64–67], many materials contain a connected-squares motif in one of their cross-sections which is responsible of their anomalous mechanical behavior. In the present case, the behavior under compression of the chains of rotating parallelograms forces the increase the dimension of the full structure along $[010]$ and the diminution of its dimension along $[100]$. Since the chains are not linked directly, the structural model differs from the rotating squares model [63] or other models based on rotating polygons as rectangles [65,68], rhombi [69] and parallelograms [70–71]. An analytical study of the properties of this model should be performed in order to analyze the variations of its mechanical properties with respect to the variations in the structural parameters of the model such as the length of the edges of the parallelograms, their internal angle and the distances between the chains.

Fig. 3. Views of $3 \times 3 \times 2$ supercells of the computed crystal structures of silver oxalate [1] under isotropic pressures $P = -0.394$ GPa and $P = -0.127$ GPa: (A) yz plane; (B) xz plane; (C) Isolated chains of rotating parallelograms. Color code: Ag – Clear blue; C – Gray; O – Red.

Conclusions

In this work, the X-ray diffraction patterns of a powdered crystalline sample of silver oxalate under pressure were measured at room temperature in the Beijing Synchrotron Radiation Facility. From the X-ray powder patterns, the lattice parameters of the crystal structure of this material under different isotropic pressures were extracted. The analysis of these parameters revealed the extremely anomalous mechanical behavior of this material. The unit cell of silver oxalate increases along the directions of two of its principal axes under compression and, therefore, silver oxalate exhibits the highly infrequent negative area compressibility phenomenon. The compressibilities along these two directions are not only negative but also very large in absolute value. Silver oxalate presents the more extreme NAC effect found so far.

These results constitute an experimental verification of the negative linear compressibility effect predicted earlier for silver oxalate using first principles solid state methods [1]. The prediction was made for silver oxalate at zero temperature, but the NLC effect in this material persists at room temperature. Therefore, the first principles methodology allows to perform accurate predictions of the mechanical properties of solid materials. At the same time, the accuracy of these methods for mechanical property prediction probes their validity for the interpretation and visualization of the deformation of the structures under pressure at the microscopic scale, being a powerful tool for unveiling the mechanisms leading to the presence of anomalous mechanical phenomena in solid materials. An inspection of the computed crystal structures of silver oxalate under pressure, reveals that the negative compressibility mechanism in silver oxalate can be rationalized in terms of a “chains of rotating parallelograms” structural model.

Appendix A. Determination of the lattice parameters of silver oxalate

For crystalline systems with monoclinic space symmetry, the position of the reflections with indices $[h00]$, $[0k0]$, $[0kl]$ and $[hkl]$ are given by [72]:

$$d[h00] = \frac{a}{h} \sin \beta \quad (\text{A.1})$$

$$d[0k0] = \frac{b}{k} \quad (\text{A.2})$$

$$d[0kl] = \left(\frac{k^2}{b^2} + \frac{l^2}{(c \sin \beta)^2} \right)^{-\frac{1}{2}} \quad (\text{A.3})$$

$$d[hkl] = \left(\frac{h^2}{(a \sin \beta)^2} + \frac{k^2}{b^2} + \frac{l^2}{(c \sin \beta)^2} - \frac{2hl \cos \beta}{(a \sin \beta)(a \sin \beta)} \right)^{-\frac{1}{2}} \quad (\text{A.4})$$

From the positions of the $[020]$, $[100]$, $[011]$ and $[-1-11]$ reflections, one can determine all the lattice parameters. From (A.2), we can obtain b :

$$b = 2 \cdot d[020] \quad (\text{A.5})$$

and from (A.1), we can determine $a \sin \beta$ using:

$$as \equiv a \sin \beta = d[100] \quad (\text{A.6})$$

Now from (A.3), since b is known, one can obtain $c \sin \beta$:

$$cs \equiv c \sin \beta = \left(\frac{1}{d[011]^2} - \frac{1}{b^2} \right)^{-\frac{1}{2}} \quad (\text{A.7})$$

Finally, from (A.4) we obtain $\cos \beta$ (and β itself),

$$\cos \beta = \frac{as \cdot cs}{2} \left(\frac{1}{d[-1-11]^2} - \frac{1}{b^2} - \frac{1}{as^2} - \frac{1}{cs^2} \right) \quad (\text{A.8})$$

The determination of a and c from as , bs and β is obvious.

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Compliance with Ethical Standards

Conflict of Interest: The authors declare that they have no conflict of interest.

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