Materials and Devices
An International Scientific Journal
OPEN ACCESS Freely Accessible Scientific Papers.
CA-IP
Managed by scientists for Science - http://co-ac.com

Article type: A-Regular research paper

Theoretical study of structural phase transition and soft mode behavior in moganite

M. Smirnov (1), D. Pankin (2), E. Roginskii (3), A. Povolotckaia (4)

(1) Faculty of Physics, St. Petersburg State University, Russia, m.smirnov@spbu.ru
(2) Center for optical and laser materials research, St. Petersburg State University, Russia, dmitrii.pankin@spbu.ru
(3) Laboratory of Spectroscopy of Solid State, Ioffe Institute, Russia, e.roginskii@mail.ioffe.ru
(4) Center for optical and laser materials research, St. Petersburg State University, Russia, anastasia.povolotckaia@spbu.ru

Corresponding author : m.smirnov@spbu.ru

RECEIVED: 28 December 2023/ RECEIVED IN FINAL FORM: 28 january 2024/ ACCEPTED: 2 February 2024

Abstract : Changes in the structure and lattice dynamics of the moganite during crystal expansion were studied using ab initio calculations within the framework of density functional theory. The results obtained shed light on many anomalies in the temperature behavior of this crystal, such as the presence of a phase transition, soft mode condensation, elastic anomalies and negative thermal expansion. Comparison of the structural and dynamic properties of moganite and quartz opens up new possibilities for their identification in natural samples of mixed composition.

Keywords : SILICA, MOGANITE, PHASE TRANSITION

Cite this article: M. Smirnov, D. Pankin, E. Roginskii, A. Povolotckaia, OAJ Materials and Devices, vol 7, p 1228-1 (2023) - *DOI: 10.23647/ca.md20231228*

I. Introduction

Moganite is a relatively recently discovered but widespread polymorph of silica, commonly intergrown with quartz in natural microcrystalline silica samples [1]. Crystallographers claim that almost every diffraction pattern obtained on microcrystalline quartz samples contains some peaks that can only be attributed to moganite [2]. To our knowledge, there have been no reports of successful synthesis of moganite single crystals so far. However, despite initial skepticism about the differences between moganite and quartz, the International Commission on New Minerals approved moganite as a distinct mineral species in 1999. Calorimetric studies have shown that the enthalpy of moganite with respect to quartz is 3.4 ± 0.7 kJ/mol, which is slightly higher than that of tridymite and cristobalite [3]. Consequently, moganite is a metastable state of silica and upon long-term exposure (more than 100 million years) it is diagenetically transformed into quartz [4].

The X-ray [4] and Raman [5] studies of powder samples of quartz-moganite mixtures have shown that, like other polymorphic modifications of silica (quartz, cristobalite, tridymite), moganite undergoes a reversible phase transition

Table 1. Unit cell parameters of α and β-moganite

Parameters	α-moganite *I*2/*a*		β-moganite *Imcb*		
	Exp. T=298 K	Calc. P=0	Exp. T=570 K	Calc. P=0	Calc. $P=P_c$
a (Å)	8.711	8.5222	8.133	8.758	8.911
b (Å)	4.863	4.7675	4.890	4.876	4.984
c (Å)	10.714	10.5895	10.735	10.715	10.879
β (°)	90.19	90.12	90	90	90
V (Å^3/SiO$_2$)	37.83	35.96	38.56	37.14	40.28

Table 2-1. Atomic positions in α-moganite (*I*2/*a*)

	Exp. T= 298 K			Calc. P=0		
Si1	1/4	0.9726	0	1/4	0.96574	0
Si2	0.0103	0.2486	0.1682	0.01534	0.29534	0.16564
O1	0.9781	0.0644	0.2878	0.97829	0.11483	0.29169
O2	0.1678	0.1708	0.1002	0.17034	0.16721	0.10384
O3	0.8703	0.2296	0.0675	0.87842	0.22505	0.06816
	x	*y*	*z*	*x*	*y*	*z*

Table 2-2. Atomic positions in β-moganite (*Imcb*)

	Exp. T=1354 K			Calc. P=0			Calc. $P=P_c$		
Si1	¼	0	0	¼	0	0	¼	0	0
Si2	0	0.2255	0.1701	0	0.2691	0.1664	0	0.2314	0.1670
O1	0	0.0416	0.2935	0	0.0985	0.2978	0	0.0330	0.2834
O2	0.1471	0.2007	0.0824	0.1479	0.1992	0.0866	0.1471	0.1869	0.0849

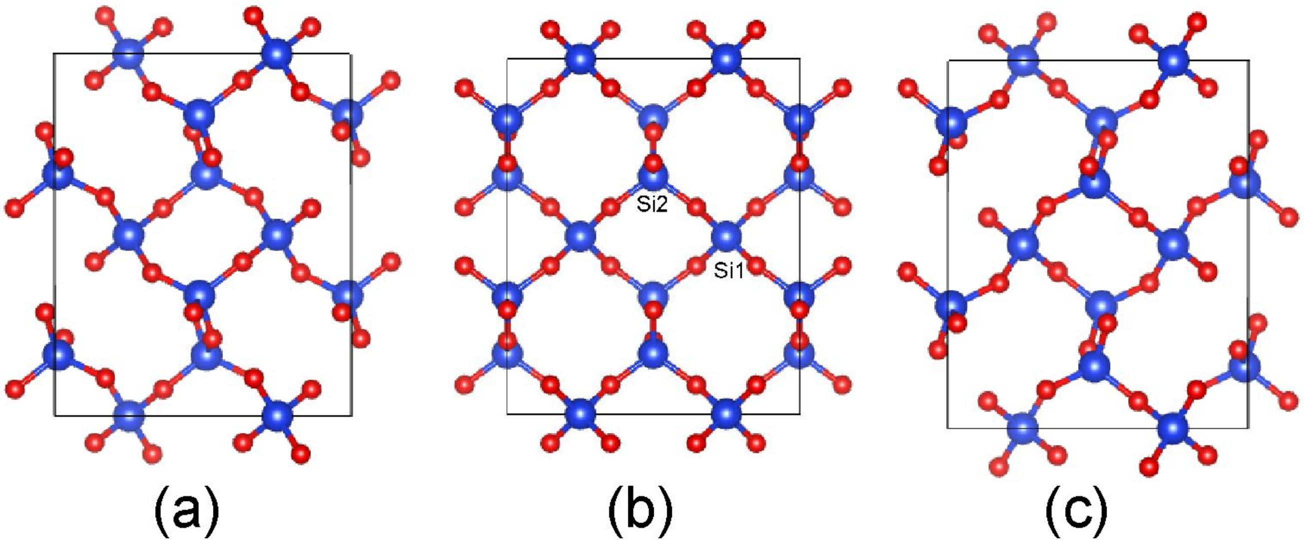

Figure 1: Structures of two moganite phases shown in *ac*-projection: α-moganite (a, c) , β-moganite (b).

at elevated temperatures. This transition is accompanied by a number of anomalies: condensation of the soft mode, an abrupt change in elastic constants, and the appearance of negative thermal expansion. The existence of high-temperature SPT in moganite does not seem to be an anomaly - similar structural transformations were observed in many silica polymorphs (quartz, cristobalite, tridymite). All these SFPs have been the subject of detailed studies, both experimental and theoretical. Regarding SPT in moganite, only two works have been published so far, containing an analysis of experimental data: X-ray diffraction [4] and Raman spectroscopy [5]. This paper presents the results of a theoretical study of the SPT mechanism in moganite. In view of the structural similarity of moganite and quartz and their inevitable coexistence in natural silica samples, the task of their identification becomes very urgent. The effectiveness of IR spectroscopy has been demonstrated in this regard [6]. Additional information about the composition and structure of quartz-moganite samples can be obtained from a comparison of the anomalies accompanying the SPT in both crystals. This paper presents the results of a theoretical study of structural, dynamic and elastic anomalies during SPT in moganite in comparison with similar phenomena in quartz.

Since the SPT we are considering is associated with the transformation of a monoclinic cell into an orthogonal one, we can choose the value of the monoclinic angle as an order parameter.

Comparing the positions of atoms in the cells of two phases, one can see 4 more combinations, which can also serve as an order parameter

$$1-y(\mathrm{Si1}),\ \ x(\mathrm{Si2}),\ 1-x(\mathrm{O1}),\ 1-\left(x(\mathrm{O2})-x(\mathrm{O3})\right) \qquad (1)$$

The structures of the two phases are shown in Fig. 1. It can be seen that their main difference is the rotation of Si1 tetrahedra and Si2 chains relative to the *b* axis. As in any SPT of the second kind, there are two configurations of low-symmetrical phases $\alpha1$ and $\alpha2$, differing in the sign of rotation (compare Figs. 1a and 1c). If we assume that the atomic positions given in Table 2-1 correspond to $\alpha1$, then the atomic positions in the structure $\alpha2$ will differ in the sign of the combinations listed in eq. (1).

II. Computational details

The calculation was performed in the Castep software (Material Studio) within the density functional theory (DFT) using the CA-PZ functional [7-9] and the norm-conserving pseudopotential. The plane wave basis cutoff energy was chosen 1000 eV. The self-consistency field (SCF) criterion was chosen to $5\cdot10^{-8}$ eV/atom. For all cases the geometry optimization procedure was performed using the LBFGS method [10] until residual forces, residual stresses and maximum ionic displacements did not exceed 0.002 eV/ Å , 0.005 GPa, 5.10^{-6} Å , respectively. The k-space integration grid was chosen according to Monkhorst-Pack scheme [11]. The dimension of the k-space grid was chosen in order to provide the step about 0.04 1/Å both for quartz and moganite structures. The above computational scheme was successfully used for studying the Raman spectrum of the moganite [12].

III. Results and discussion

Structure and energy

At low temperatures, moganite crystallizes in a monoclinic structure with space group *I*2/*a* (α-moganite). When heated above 570 K, the structure becomes orthorhombic with space group *Imcb* (β-moganite). The structural parameters of the cells of two phases of moganite, obtained in our calculations, are given in Table 1 in comparison with experimental data [2]. The positions of atoms in the cells of α-moganite and β-moganite are given in Tables 2-1 and 2-2, respectively.

The calculation scheme we use, based on the harmonic approximation, does not allow us to directly study the behavior of the crystal at elevated temperatures. However, it is possible to model this behavior by considering the evolution of the system with increasing volume or, equivalently, under the influence of external negative pressure. Of course, with this approach there is no possibility of studying the amplitude factor - the influence of the amplitudes of atomic vibrations on the crystal structure, but it remains possible to study the volume factor - the influence of the lattice expansion on the structure, energy, phonon spectrum and elastic constants of the crystal, while remaining within the framework of the quasi-harmonic approximation. This approach was successfully used in studies of high-temperature SPTs in quartz and cristobalite [13-16]. The application of a similar approach to moganite forms the basis of this study.

We performed a series of calculations, optimizing the structures of the two phases at various values (both positive and negative) of external pressure. The results of calculations at positive pressures can be compared with data from experimental studies of a crystal under hydrostatic compression. The results of calculations at negative pressures can be compared with experimental data on thermal expansion. Note that the problem of optimizing a structure for a given external pressure is equivalent to the problem of optimizing a structure for a given volume. The dependences of the energies of two moganite phases on the lattice volume, calculated using the calculation scheme we have chosen, are shown in Fig. 2.

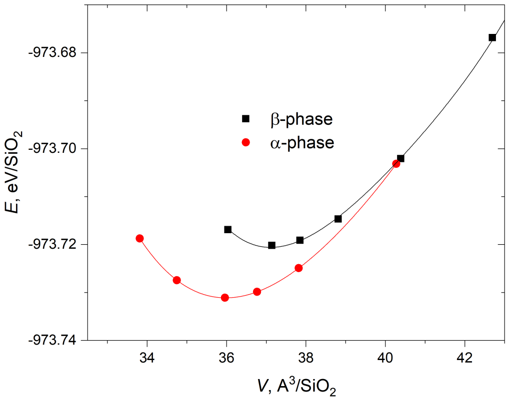

Figure 2: Energy versus volume dependences for α and β-phases of moganite.

It can be seen that as the volume increases, the *E*(*V*) curves come closer and merge at the value $V=V_c$. At the same point, the parameters of the cells of the two phases take equal values, and the combinations of positional parameters listed in eq. (1) become zero. This behavior indicates the presence of a second-order SPT: with an adiabatic increase in volume, α-moganite transforms into β-moganite. According to our calculations, the value $V=V_c$ corresponds to the external pressure P_c= -1.5 GPa. The structure parameters at the critical point are given in Tables 1. 2-2.

Let us recall that each point on these curves was obtained by complete optimization of the structure with a given symmetry group at a fixed value of external pressure. It can be seen that both dependences have the form of curves with clearly defined minima, which correspond to structures at P=0 and T=0. For each fixed value of V, the energy difference between the two phases corresponds to the height of the energy barrier separating the minima α1 and α2. At the point $V=V_c$ the curves smoothly merge, and the height of the energy barrier becomes zero.

According to our calculations, the value of V_c at which SPT occurs is 12% greater than the volume of the α-phase at P = 0 and T = 0, and in the experiment SPT occurs at V increased by only 2% relative to the volume at P = 0 and T = 300K. This discrepancy can partly be attributed to the effect of thermal expansion of the α-phase upon heating from 0 to 300 K. On the other hand, this discrepancy can be explained by the fact that our calculations did not take into account the amplitude factor. According to Fig. 2, the height of the energy barrier separating the points of the potential surface corresponding to the two phases is equal to 0.01 eV/SiO_2, which is equivalent to the thermal energy at T = 116 K. Consequently, even at room temperature, the atoms in the moganite lattice have enough kinetic energy to overcome such a barrier. It is quite possible that in the samples studied in [4], the moganite grains were in a compressed state. In this case, the height of the energy barrier is much higher, and phase transition occurs at higher temperature.

Soft-mode behavior

The structural changes shown in Fig. 1 indicate that the SPT in moganite belongs to the “displacement” type transitions. Consequently, a soft mode, whose frequency vanishes at the transition point, must exist in the phonon spectrum of both phases. Since the SPT occurs without changing the number of atoms in the cell, this mode must belong to the center of the Brillouin zone. In addition, according to group theory, the soft mode must belong to the fully symmetric irreducible representation (IR) of the symmetry group of the low-symmetry phase. The distributions of zone-center phonons over the IRs of the two phases and the correlation between them are presented in Table 3.

From the above diagram of correlations between the IRs of two structures it follows that the SM should belong to the A_g type in the low-symmetry phase and the B_{2g} type in the high-symmetry phase. Indeed, in the phonon spectra of the two structures we calculated, there are modes whose frequencies vanish at $P=P_c$. The dependence of the frequency of these modes on external pressure is shown in Fig. 3.

Table 3. Correlated distributions of zone-center phonon modes by irreducible representations in α and β-phases of moganite

α-phase, *I*2/*a*	β-phase, *Imcb*
$13\mathbf{A_g}$	$7A_g+6\mathbf{B_{2g}}$
$14\mathbf{B_g}$	$\mathbf{6B_{1g}}+8B_{3g}$
$13A_u$	$5A_u+8B_{2u}$
$14B_u$	$8B_{1u}+6B_{2u}$

In the phonon spectrum of moganite that we calculated, there is another mode, the frequency of which exhibits the same dependence on volume: it decreases in the α-phase and increases in the β-phase. This mode belongs to the Bg IR in the α-phase and becomes the B_{1g} mode in the β-phase. However, in contrast to the soft A_g-B_{2g} mode discussed above, the frequency of the B_g-B_{1g} mode, although becomes very small (32 cm^{-1}) but does not go to zero at the critical point.

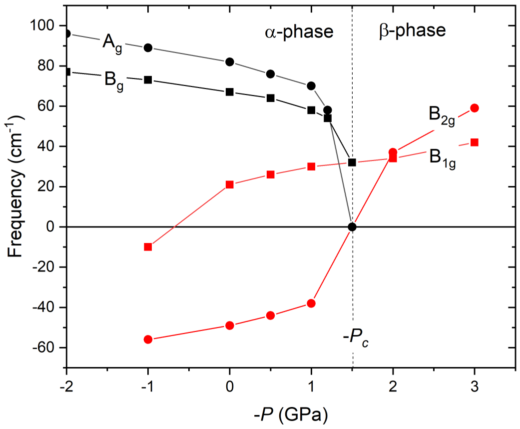

Figure 3: Frequency versus negative pressure dependences for soft modes in moganite.

According to the calculated eigenvectors, the B_{1g} mode is in no way related to the soft B_{2g} mode. The B_{2g} mode consists of antiphase tilts of Si1 tetrahedra and Si2 chains around the *b* axis. The B_{1g} mode consists of bends of Si2 chains around the same axes and translations of Si1 tetrahedra in the direction of the c axis. If the role of the soft mode were played by the B_{1g} mode, then the symmetry group of the low-temperature phase would be C2/c (#15).

Both modes discussed are active in the Raman spectrum. However, they were not observed in the spectrum of moganite, since the Raman spectra of this crystal were not measured in the low-frequency region. But in the $AlPO_4$ crystal isostructural to moganite, for which such measurements were carried out, two low-frequency modes of A_g and B_g symmetry were discovered in the low-temperature phase [17].

IV. Conclusion

The stability of the experimentally established structure of α-moganite was confirmed theoretically using quantum mechanical calculations within the framework of DFT. It is shown that the calculated structural parameters are in good agreement with experiment. Monitoring changes in the structure and phonon spectrum of this crystal during lattice expansion made it possible to detect the presence of a soft mode, the frequency of which vanishes with a certain critical increase in volume and begins to increase with a further increase in volume. It is shown that at the critical point the lattice transforms from monoclinic to orthorhombic, and the symmetry group of the crystal changes from *I*2/*a* to *Imcb*. All these metamorphoses are consistent with the experimentally observed SPT of α-moganite into β-moganite, which occurs upon heating to 570 K. Moreover, the calculation results confirmed that the soft mode eigenvector coincides with the pattern of atomic displacements during SPT. In α-moganite, the soft mode belongs to the B_{2g} representation and interacts with shear deformation in the *ac* plane. The vanishing of the frequency of this mode inevitably entails the vanishing of the elastic constant shear strain and the transformation of the orthorhombic lattice into a monoclinic one. Thus, we can classify moganite as an improper ferroelastic.

Another mode was discovered in the phonon spectrum of moganite, the frequency of which decreases along with lattice expansion to 32 cm^{-1} in the low-temperature phase, and then begins to increase in the high-temperature phase. This mode belongs to the B_{1g} representation and interacts with the shear deformation in the *ab* plane. This quasi-soft mode behavior can be considered as a potential prerequisite for the transformation of a monoclinic lattice into a triclinic one.

A comparison of moganite and quartz showed their similarity both in density and in the energy of formation. The main peculiarity of moganite is the presence of 4-membered rings of Si-O-Si bridges, which explains the somewhat higher enthalpy of moganite. A comparison of the α-β phase transformations in quartz and moganite showed that in moganite the SPT occurs at a smaller volume increase and with overcoming a lower barrier, which is reflected in a lower transition temperature and a lower frequency of the soft mode.

REFERENCES

1. O. W. Florke, J. B. Jones, H.-U. Schminke. *Z. Kristallogr*. **vol. 143**, p 156 (1976)
2. P J. Heaney, J. E. Post. *Science* **vol. 255**, p 441 (1992)
3. I. Petrovic, P. J. Heaney, A. Navrotsky. *Physics and Chemistry of Minerals* **vol. 23**, p 119 (1996)
4. P J. Heaney, J. E. Post. *American Mineralogist* **vol. 86**, p 1358 (2001)
5. P. J. Heaney, D. A. McKeown, and J. E. Post. *American Mineralogist* **vol. 92**, p 631 (2007)
6. M. Zhang, T. Moxon. *American Mineralogist* **vol. 99**, p 671 (2014)
7. D.M. Ceperley, B.J. Alder, *Phys. Rev. Lett.* **vol. 45**, p 566 (1980)
8. J. P Perdew, *Proceedings of the AIP Conference Proceedings; AIP*, p 1 (2001)
9. J. P Perdew,.; Zunger, A. *Phys. Rev. B* **vol. 23**, p 5048 (1981)
10. J. Aarons, A New CASTEP and Onetep Geometry Optimiser (2011)
11. H.J.Monkhorst, J.D. Pack. *Phys. Rev. B* **vol. 13**, p 5188 (1976)
12. D. Pankin, M. Smirnov, E. Roginskii, A. Savin, I. Kolesnikov, A. Povolotckaia, *Photonics*, **vol.10**, p 1346 (2023)
13. B. Silvi, P. D'Arco, and M. Causa, *J. Chem. Phys*. **vol.** 93, p 7225 (1990)
14. F. Liu, S. H. Grafolani, D. King-Smith, and D. Vanderbilt *Phys. Rev. Lett.* **vol. 70**, p 2750 (1993)
15. F. Liu, S. H. Grafolani, D. King-Smith, and D. Vanderbilt, *Phys. Rev. B* **vol. 49**, p 12 528 (1994)
16. M. B. Smirnov and A. P. Mirgorodsky, *Phys. Rev. Lett.* **vol. 78**, p 2413 (1997)
17. M. Kanzaki. *J. Miner. Petr. Sci*. **vol. 113**, p 126 (2018)

Important: Articles are published under the responsability of authors, in particular concerning the respect of copyrights. Readers are aware that the contents of published articles may involve hazardous experiments if reproduced; the reproduction of experimental procedures described in articles is under the responsability of readers and their own analysis of potential danger.

Reprint freely distributable – Open access article

Permissions – Important: all materials in this article may be freely reused (figures, tables, …) without any need to ask permission or to pay any fee. It is simply asked to refer to the article.

Materials and Devices is an Open Access journal which publishes original, and **peer-reviewed** papers accessible only via internet, freely for all. Your published article can be freely downloaded, and self archiving of your paper is allowed and encouraged! Put your article as soon as possible on your personal sites, institutional sites, etc!

We apply « **the principles of transparency and best practice in scholarly publishing** » as defined by the Committee on Publication Ethics (COPE), the Directory of Open Access Journals (DOAJ), and the Open Access Scholarly Publishers Organization (OASPA). The journal has been designed so that it can be accepted by DOAJ, and we are happy to inform you that this is the case now.

Copyright on any article in Materials and Devices is retained by the author(s) under the Creative Commons (Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0)), which is favourable to authors.

Aims and Scope of the journal : the topics covered by the journal are wide, Materials and Devices aims at publishing papers on all aspects related to materials (including experimental techniques and methods), and devices in a wide sense provided they integrate specific materials. Works in relation with sustainable development are welcome. The journal publishes several types of papers : A: regular papers, L : short papers, R : review papers, T : technical papers, Ur : Unexpected and « negative » results, Conf: conference papers, and O: Opinion papers. Recently we introduced a new type of articles : « Methods ».

(see details in the site of the journal: http://materialsanddevices.co-ac.com)

Important: all submitted articles, fullfilling above indications, are evaluated by peers from a pure scientific point of view! The editor-in-chief does not take any right of censorship, whether on the basis of the subject of the article, or the strength of the “profile of the authors”, their reputation, or other. We do not take any action to mechanically optimize the impact factor of the journal, for example by analyzing the forecast number of citations of the article based on the number of scientists working in the field, or fashion effects, or other.

We want to maintain Materials and Devices Open Access and free of charge thanks to volunteeriing, the journal is managed by scientists for science! You are welcome if you desire to join the team!

Advertising in our pages helps us! Companies selling scientific equipments and technologies are particularly relevant for ads in several places to inform about their products (in article pages as below, journal site, published volumes pages, …). Corporate sponsorship is also welcome!

Feel free to contact us! contact@co-ac.com