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Computer simulation of Na₂ThF₆ single crystals: prediction of a phase transition under hydrostatic pressures

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Abstract

In this work we have performed atomistic simulations for the Na₂ThF₆ compound in order to investigate the predicted ferroelastoelectric and ferrobielastic $P\bar{6}2m \rightarrow P321$ structural phase transition induced by hydrostatic pressure. The set of potentials obtained describe very well the structural parameters and dielectric constants at room temperature and pressure. On increasing pressure this phase transition occurs at around 6 GPa and has been observed from anomalous changes in several calculated observables. The elastic constant and piezoelectric coefficient tensors satisfy the symmetry criteria imposed by the $P\bar{6}2m \rightarrow P321$ ferroic phase transition.

1. Introduction

Together with other complex fluorides containing the 5f elements, Na₂ThF₆ was first investigated as part of the Manhattan project by Zachariassen [1–4], who determined its crystalline structure using x-ray diffraction experiments. The interest in these compounds arises from their potential applications in core coolants with solid fuels, liquid fuel in a molten salt reactor or solvent for spent nuclear fuel [5–7]. Besides this, Na₂ThF₆ belongs to a set of a few hexafluorometallates (A₂MF₆) that show highly coordinated polyhedra for A⁺ and M⁴⁺ ions [8]. Commonly, these compounds show octahedrally coordinated M sites [1–4]. Zachariassen [1–4] proposed several structures for the A₂MF₆ compounds. The first one, called the α -phase, is isomorphic with the fluorite structure CaF₂ ($Fm\bar{3}m$, $Z = 4$). In this structure the Na⁺ and Th⁴⁺ ions are randomly distributed over the metal sites (Ca site). The second one, called the β -phase, is trigonal, belonging to the $P321$ space group with one molecule per unit cell. This phase was also described with a basis in the $P\bar{6}2m$ group. In both proposed β structures, Na⁺ and Th⁴⁺ ions are disposed in an ordered fashion at the centers of trigonal tricapped prisms whose vertices are occupied

by fluorine ions. More recently, using x-ray diffraction, calorimetric and second-harmonic generation measurements, Grzechnik *et al* [8] have confirmed the structure at room temperature as $P321$. Moreover, they also demonstrated that this phase is stable between 290 and 954 K or under hydrostatic pressure up to 4.89 GPa. The relationship between $P321$ and $P\bar{6}2m$ space groups suggest that Na₂ThF₆ is ferrobielastic and ferroelastoelectric, where $P321$ is the high order ferroic phase and $P\bar{6}2m$ is the prototypic phase [9]. This transition was not observed by Grzechnik *et al*, but they observed that the z coordinate of the Na⁺ ion, occupying the 2d Wyckoff site ($1/2, 2/3, z$), shows a tendency to converge to the value $1/2$, which corresponds to the 2d site ($1/2, 2/3, 1/2$) of the $P\bar{6}2m$ space group, on increasing pressure. They also observed that Na₂ThF₆ presents structural twins at room temperature. These two facts are indirect evidence of the presence of this SPT under hydrostatic pressure above the experimental investigation values. Simulation methods are good tools for investigating this problem since they easily allow us to achieve pressures higher than the one obtained in the laboratory. In this work we have performed atomistic simulation for Na₂ThF₆ in order to describe its behavior under high hydrostatic pressures, including the appearance of

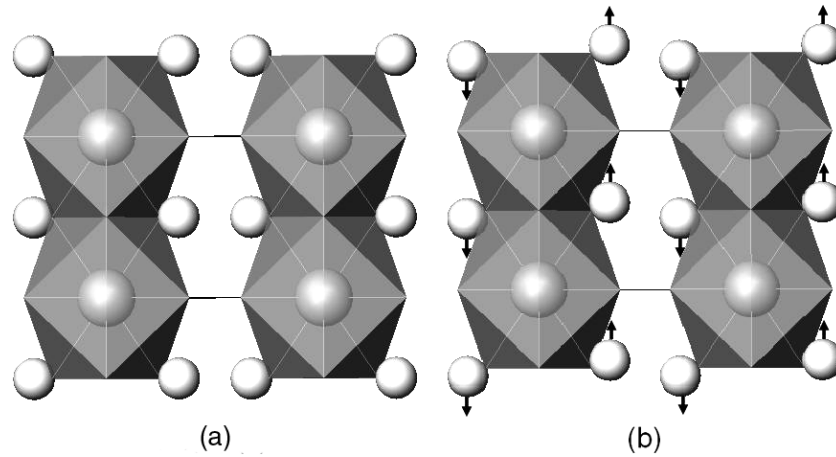


Figure 1. Comparison between the (a) prototype (predicted) and (b) ferroic (room temperature observed) structures of the Na_2ThF_6 single crystal. The view is perpendicular to the z axis.

Ferroic group $P321$			Prototype group $P\bar{6}2m$		
Ion	Site	Position		Site	Position
Na	2d	$(\frac{2}{3}, \frac{1}{3}, z_{1f})$	\longrightarrow	2d	$(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$
Th	1a	$(0, 0, 0)$	\longrightarrow	1a	$(0, 0, 0)$
F1	3e	$(x_{1f}, 0, 0)$	\longrightarrow	3f	$(x_{1p}, 0, 0)$
F2	3f	$(x_{2f}, 0, \frac{1}{2})$	\longrightarrow	3g	$(x_{2p}, 0, \frac{1}{2})$

Figure 2. Wyckoff site splitting across the $P\bar{6}2m$ to $P321$ structural modification.

the predicted elastic structural phase transitions (SPT). This simulation method has the main advantage of introducing temperature effects intrinsically to the empirical potentials, ones that fit experimental observables at finite temperatures. Moreover, this methodology has been employed successfully for describing other fluoride compounds and for modeling SPT at increasing pressure [10–15].

2. Ferroic and prototype structures

2.1. Crystalline structures and their relationships

The β -phase (the predicted ferroic phase) of the Na_2ThF_6 crystal is trigonal, belonging to the $P321$ space group with one molecule per unit cell. As discussed in the later section, in this structure each Na and Th ion occupies the center of a trigonal tricapped prism whose vertices are occupied by fluorine ions, where the NaF_9^{-8} polyhedron is more irregular than the ThF_9^{-8} polyhedron. This space group is a subgroup of the prototype $P\bar{6}2m$ space group. In this possible SPT the $P\bar{6}2m$ group loses a twofold symmetry along the z axis, leading to the $P321$ group. This is due the Na displacement along the z axis as shown in figure 1. This is the only change in the crystalline

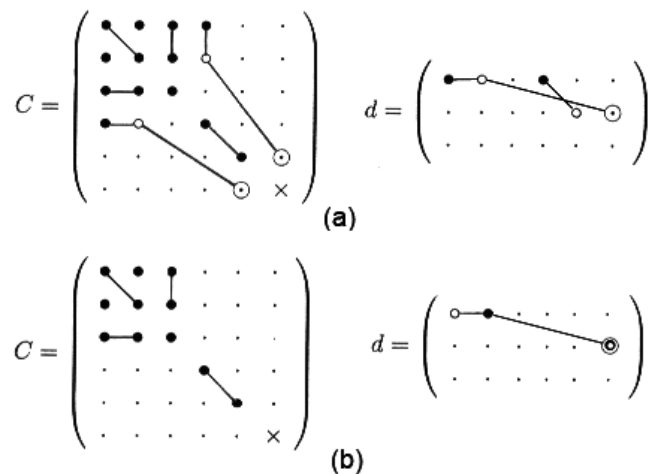


Figure 3. Independent components of the elastic constant (C) and piezoelectric (d) tensors in the (a) ferroic and (b) prototype symmetries, respectively.

structure due to the SPT, as we can see from the complete Wyckoff site splitting shown in the correlation diagram of figure 2 [16, 17].

Thus, when the $P321 \rightarrow P\bar{6}2m$ SPT occurs, the z coordinate of the Na^+ ion goes to the special position $1/2$. This tendency was observed by Grzechnik *et al* [8] and z is the most interesting parameter to be considered under increasing pressure in order to verify the SPT.

2.2. Crystalline tensorial properties

As the SPT is simultaneously ferroelastic and ferroelasto-electric, it is interesting to observe the elastic and piezoelectric tensor changes. The elastic constant C and piezoelectric d tensors of the $P321$ structures have their independent components given in figure 3, where we have employed Nye’s matrix notation [18]. Thus, we can see that the most remarkable changes in the elastic constant and piezoelectric coefficient are that the C_{14} and d_{14} components vanish at the ferroic transition.

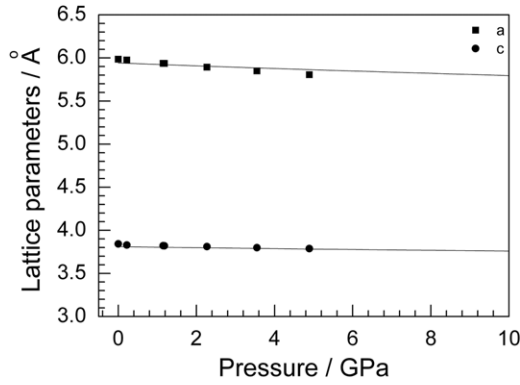


Figure 4. Pressure dependence of the simulated lattice parameters of the Na_2ThF_6 crystal. The solid lines indicate the simulation results and the symbols the experimental values [8].

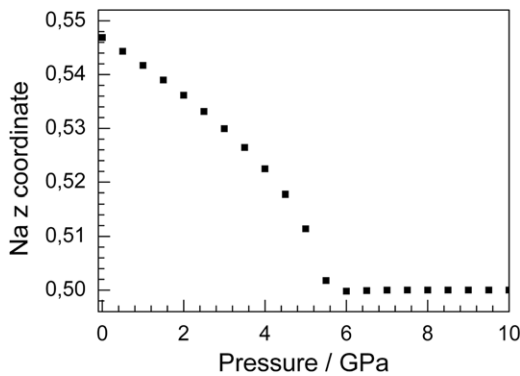


Figure 5. Pressure dependence of the simulated z coordinate of the Na ion in the Na_2ThF_6 crystal.

3. Computational method

The interactions between the ions was assumed to be of the form

$$V_{ij} = -\frac{Z_i Z_j e^2}{r_{ij}} + A \exp(-r_{ij}/\rho) - \frac{C}{r_{ij}^6} \quad (1)$$

where the index i and j label the ionic species, Z_i is the charge of the ion labeled by i in units of proton charge. In this expression, the three terms represent the Coulombic, Pauli and Van der Waals interactions, respectively.

In order to model the ions in the Na_2ThF_6 structure we have used the shell model proposed by Dick and Overhauser [19], since this model has been applied with success to describe other fluoride compounds [10–15]. In this classical model, the ion is represented by a system constituted of a massless shell with charge Y and a core with charge X , connected by a harmonic potential represented by a spring of elastic constant k (see equation (2)), giving rise to a finite ionic polarizability. It is worth noting, however, that this representation is only a parametrization, and the charges assigned to the ions, the shells and the cores do not necessarily mean the actual charges resulting from detailed electronic structure of the crystal:

$$E_{\text{core-shell}} = \frac{1}{2} k r^2. \quad (2)$$

Table 1. Potential parameters used in this work.

Short-range potential parameters			
Interaction	A (eV)	ρ (Å)	C (eV Å ⁶)
Na–F	377.385 43	0.376 656	0.0000
Th–F	3907.5051	0.304 819	0.0000
F–F	3785.7318	0.330 705	450.958 02
Shell model parameters			
Ion	k (eV Å ⁻²)	Y ($ e $)	X ($ e $)
Na	18.296 757	2.128 000	−0.381 245
Th	20 898.441	8.000 000	−3.457 628
F	28.426 373	−1.339 000	−0.000 313

Table 2. Comparison between experimental and calculated observables.

Parameter	Experimental	Calculated	Error (%)	Reference
Structural parameters				
a (Å)	5.985 00	5.941 30	0.73	[8]
c (Å)	3.843 00	3.810 34	0.85	[8]
z_{Na}	0.548 00	0.546 89	0.20	[8]
x_{F1}	0.619 00	0.619 04	<0.01	[8]
x_{F2}	0.251 00	0.250 90	0.04	[8]
Dielectric constants				
ϵ_{11}	6.953	6.945	0.12	[24]
ϵ_{33}	24.693	24.206	1.97	[24]

To perform the calculations, we have employed the GULP code [20–22] which fits the experimental data (lattice parameters and dielectric constants) by optimizing the structure with respect to the cell strains and atomic coordinates. To optimize, the program uses analytically adapted derivatives using the Newton–Raphson procedure starting from the exact Hessian matrix. More details about the algorithm used by GULP can be found elsewhere [23].

From the best fit achieved to reproduce adequately some physical properties of the Na_2ThF_6 crystals, namely dielectric constants and structural parameters, we determined the short-range interionic potentials A , ρ and C , as well as the shell parameters Y and k of the fluorine ions.

4. Results and discussion

4.1. Potential parameters

The potential parameters were set to fit the experimental structural and dielectric parameters of the Na_2ThF_6 single crystals. The potential parameters adopted are given in table 1.

The good reliability of the potentials adopted is observed from the comparison between the experimental and calculated observables given in table 2. In particular, the dielectric constants calculated agree well with experimental data. Since these parameters are obtained through a second-derivative matrix, these small errors reflect a good potential set [20–22].

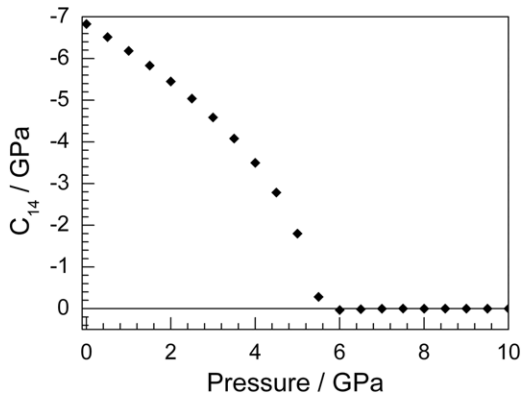


Figure 6. Pressure dependence of the simulated C_{14} component of the elastic constant tensor of the Na_2ThF_6 crystal.

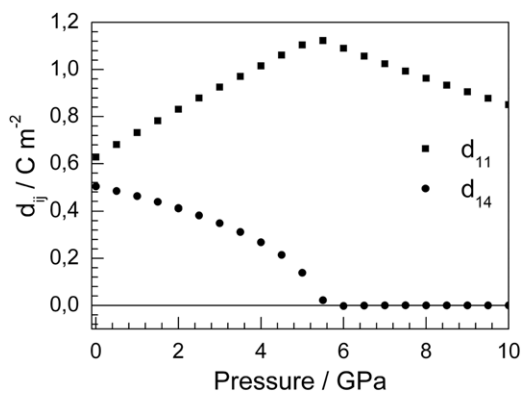


Figure 7. Pressure dependence of the simulated d_{14} component of the piezoelectric coefficient tensor of the Na_2ThF_6 crystal.

4.2. Structural phase transition

In order to observe the pressure effects on crystalline structure, we have performed the optimization of the structure from room pressure to 20 GPa in steps of 0.5 GPa. The dependence of the lattice parameters on the pressure is shown in figure 4. The good reliability of the potentials is seen again from the very good reproduction of the experimental results.

In order to emphasize the SPT we have plotted in figure 5 the pressure dependence of the z coordinate of the

Na ion. As we can see, this coordinate goes to 1/2 at around 6 GPa indicating the presence of the predicted ferroic SPT in Na_2ThF_6 single crystals. The symmetry of the high pressure phase was verified using the missing symmetry algorithm implemented in the Platon code. These calculations allow us to confirm that the hydrostatic pressure induces the $P\bar{6}2m$ predicted structure. It is important to notice that above 6 GPa, all the parameters of the atmospheric pressure phase have remained as free parameters. Thus, the prototype $P\bar{6}2m$ structure is a natural minimum of the free energy at high pressures, even though the system is allowed to relax under other conformations. In order to confirm the ferroelastic and ferroelastoelectric character of the SPT we have investigated the pressure dependence of the C_{14} and d_{14} components of the elastic constant and piezoelectric coefficient tensors, respectively; these are shown in figures 6 and 7, respectively. We can see that both vanish at around 6 GPa indicating the ferroelastic and ferroelastoelectric phase transition between the $P321$ and $P\bar{6}2m$ groups. It is interesting to note that the d_{11} component of the piezoelectric coefficient tensor also shows an anomaly at the transition showing a maximum. The SPT is observed in the anomalous behavior of other observables with increasing pressure, such as the dielectric constant and Young, shear and bulk moduli. For example, in figure 8 we show the other simulated elastic constants. We can observe that the components C_{12} and C_{13} are approximately the same before the transition and are different after the transition, as predicted from symmetry for $P321 \rightarrow P\bar{6}2m$ (see figure 8).

5. Conclusions

The static simulation of the Na_2ThF_6 crystal under hydrostatic pressure indicates that this compound shows the predicted simultaneous ferroelastic and ferroelastoelectric $P321 \rightarrow P\bar{6}2m$ phase transition at around 6 GPa. The set of potentials obtained used in the simulation describe very well the structure even under pressure changes, as well as the dielectric constant tensor at room conditions. The calculated elastic constant and piezoelectric tensors obey the symmetry imposed by the $P321 \rightarrow P\bar{6}2m$ SPT. Finally, several observables show the phase transition.

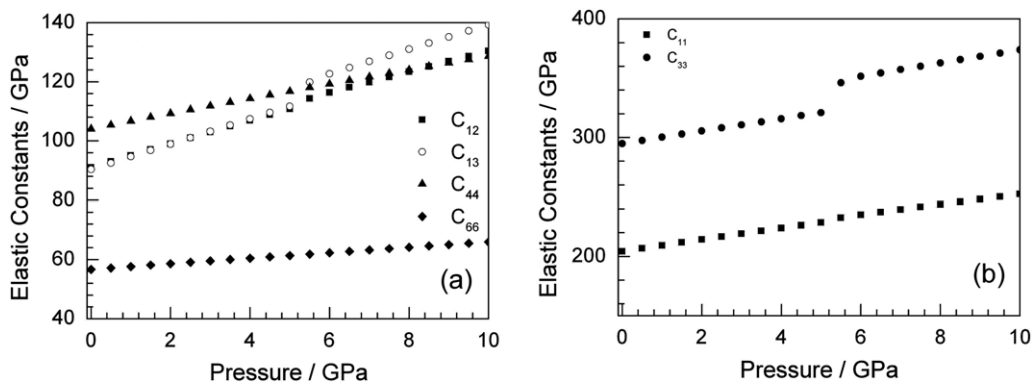


Figure 8. Pressure dependence of the rest of the simulated C_{ij} components of the elastic constant tensor of the Na_2ThF_6 crystal.

Acknowledgments

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