Computational modelling studies for high temperature monazite systems

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Abstract

Monazite is widely considered as a potential source of fissile feedstock for nuclear power generation, as it generally contains significant quantity of thorium (Th), uranium (U) and rare earth elements (REEs) within the mineral ore structure. Currently, a new process of high-temperature cracking of monazite is under development to improve the liberation of these cations from the robust monazite lattice. The current process for extraction of the REEs from the mineral involves complicated processes which makes use of harsh chemicals. These process therefore has significant scope for optimisation. With this in mind, the stability of monazite systems, t-$CeSiO_4$ and m-$LaSiO_4$ was investigated using first-principle calculation employing density functional theory (DFT) to gain a better understanding of the inherent molecular structures and the influence of temperature on conformation. The calculated lattice parameters for the model of t-$CeSiO_4$ were found to be in good agreement with the experimental values (within 3%) and deemed a sufficient m-$LaSiO_4$ of the system to be exposed to simulated reaction conditions. The elastic properties suggested that t-$CeSiO_4$ is the more stable structure compared to m-$LaSiO_4$ structure at 0 K. Semi-empirical embedded atom method interatomic potentials incorporated in the LAMMPS code were also employed to investigate the lattice expansion of t-$CeSiO_4$ at high temperatures. It was found that calculated a and b lattice parameters expand with a linear ratio to a temperature of 2200 K whereas the c parameter was found to contract in the same temperature range. The findings provided an in depth understanding of the monazite molecular structure change at higher temperatures that may be helpful in plasma cracking optimisation experimental methodologies.

Keywords: Monazite, LAMMPS code, Lattice expansion, Stability

1. Introduction

Monazite [Ce, La, Nd, Th (PO_4, SiO_4)] is an important mineral in the mining industry and contains non-trivial amounts of rare earth elements (REE), thorium (Th) and uranium (U) (Richter *et al.,* 2019). These components (REE, Th, and U) are exceptionally significant and find application in numerous areas of modern technology. The phosphate mineral exists in three common forms, monazite-(Ce), monazite-(La) and monazite-(Nd) (Santos *et al.,* 2018) and is known to be chemically very stable and highly inert (Kemp and Cilliers, 2016). It has an extremely broad range of chemical compositions reflecting ore formation in a wide variety of rock types under variable conditions. These conformations form under differing pressure and temperature environment in sedimentary, metamorphic and igneous rocks (Hoshino *et al.,* 2016). The constituent elements of monazite can be used in a wide variety of applications including catalysis, metallurgy, glass/polishing and magnetic sector (Catlos *et al.,* 2008).

It has been well-documented that the use of conventional chemical processes to extract the REEs, thorium and uranium from monazite has developed into a highly complicated and costly exercise (Kemp and Cilliers, 2016). Hence, computational modelling offers an opportunity to simulate these labour intensive experiments in a more effective and less costly manner. Accordingly, we used representative models and simulated reaction conditions to assist in to understanding how we could best extract these REEs by gaining insight into structural conformations at elevated temperatures. In this paper, the high temperature cracking of monazite systems, using a Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to investigate the lattice expansion at high temperatures was evaluated. In addition, we also calculated the heats of formation to predict thermodynamic stability, as well as the elastic constants to predict the mechanical stability, ductility and brittleness of the systems at zero temperature. More importantly, it was established that the monazite mineral showed improved strength at a temperature below the melting point.

2. Methodology

The required calculations were performed using the Vienna ab initio simulation package (VASP) code (Kresse and Hafner, 1993), based on the density functional theory (DFT). The exchange-correlation interaction was evaluated with the generalized gradient approximation (GGA) (Kohn and Sham, 1965) of Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996). A plane wave cutoff energy of 500 eV and k-point mesh of 12x12x11 for t-$CeSiO_4$ and 12x10x11 for m-$LaSiO_4$, respectively, were used to converge the total energy of the structures. Optimization of structural parameters was obtained by minimization of forces and stress tensors. The elastic constants were calculated for a small strain of 0.003. The semi-empirical embedded atom method (EAM) (Daw and Baskes, 1984) incorporated in LAMMPS code (Plimpton, 1995) was employed to investigate the lattice expansion of $CeSiO_4$ at high

temperatures. An 8x8x8 supercell of $CeSiO_4$ containing 1024 atoms was used. The temperature was varied from 400 to 2200 K. The isobaric-isothermal NPT ensemble was chosen with 100 ps simulation time and timestep of 2 fs.

3. Results and Discussion

3.1 Structures and thermodynamic properties

Table 1 lists the calculated and experimental lattice parameters, as well as the heats of formation for the optimised structures of (t-$CeSiO_4$ and m-$LaSiO_4$). The results of equilibrium lattice parameters were in good agreement with available experimental values (to within 5 %) (Kamal and Francesca, 2019).

The thermodynamic stability of these systems can be deduced from the heats of formation (ΔH_f) calculations. In order for a structure to be confirmed as the most stable configuration, the ΔH_f must have the lowest possible value (generally $\Delta H_f < 0$), where any value larger than this, implies instability.

The following expression estimates the heats of formation (ΔH_f):

$$\Delta H_f = E_C - \sum_i x_i E_i \qquad (1)$$

where E_C is the calculated total energy of the compound and E_i is the calculated total energy of each element in the compound.

When directly comparing the ΔH_f values of the candidate compounds within the scope of this study, t-$CeSiO_4$ was found to be more stable (-2.0740 eV/atom) while m-$LaSiO_4$ (-1.9500 eV/atom) highlighted a less stable structure configuration, as noted in Table 1.

3.2 Elastic properties at 0 K

The calculation of elastic constants is essential for determining and quantifying the macroscopic mechanical properties that define the mechanical inherent stability of compounds. Note that the stability criterion for the elastic constants must be satisfied in order for the structure to be defined as stable.

The mechanical stability condition for tetragonal system (Mehl and Klein, 1994) is as follows:

$c_{44}>0$, $c_{66}>0$, $c_{11}>0$, $c_{33}>0$, $c_{11}-c_{12}>0$, $(c_{11}+c_{33}-2c_{13})>0$, $2(c_{11}+c_3+2c_{12}+4c_{13})>0$ (2)

For monoclinic crystal stability condition, outlined (Bao *et al.,* 2010) is as follows:

$c_{11}>0$, $c_{22}>0$, $c_{33}>0$, $c_{44}>0$, $c_{55}>0$, $c_{66}>0$, $(c_{22}+c_{33}-2c_{23})>0$, (3)

Table 2 show the elastic constants and elastic shear moduli of the candidate monazite structures. Note that m-$LaSiO_4$ is deemed to be mechanically unstable since it notes negative values of c_{25} and

c_{46}, implying that the monoclinic stability criteria are not satisfied. In the case of t-$CeSiO_4$, the tetragonal stability criteria are satisfied and it is deemed the more stable structure as it has the highest C'.

The calculated bulk, shear, and young modulus for the monazite systems are shown in Table 3. Elastic moduli is only shown for Voigt approximation, with the calculated values being very close to the experimental results for t-$CeSiO_4$ ($\pm$ 3 % error)(Kamal *et al.,* 2019). It is seen that the t-$CeSO_4$ structure has large value of bulk, shear and young's modulus indicating that the compound is hard, with a high degree of stiffness and is not easily compressed.

Furthermore, we calculated the ratio of bulk modulus to shear modulus (B/G) to investigate the extent of fracture range in these structures. Pugh (1954) proposed that materials are considered to be ductile if the value of Pugh's criterion (B/G) > 1.75. It is observed that calculated B/G ratio is greater than 1.75 for both the t-$CeSiO_4$ and m-$LaSiO_4$ structures, signifying ductile behaviour. In order to substantiate this even further, the Poisson ratio (σ) was calculated and considered as ductile if (σ) > 0.26 (Frantsevich and Voronov, 1983). When considering the information in Table 3 it is clearly seen that the Poisson's ratio for both compounds is > 0.26, further confirming the ductile nature of t-$CeSiO_4$ and m-$LaSiO_4$.

Table 2: Elastic constants (C_{ij}), and elastic shear modulus (C') of t-$CeSiO_4$ and m-$LaSiO_4$ structures at 0 K

Elastic Constant C_{ij} (Gpa)	t-$CeSiO_4$	m-$LaSiO_4$
c_{11}	256.89	187.84
c_{12}	41.42	61.92
c_{13}	107.35	61.73
c_{15}	-	5.50
c_{22}	-	197.65
c_{23}	-	85.90
c_{25}	-	-5.77
c_{33}	336.36	172.53
c_{35}	-	5.29
c_{44}	61.47	42.35
c_{46}	-	-6.76
c_{55}	-	33.80
c_{66}	26.22	32.94
C'	215.47	62.65

3.3 Lattice expansion

In an attempt to gain a better understanding of the effects of temperature manipulations on the more stable t-$CeSiO_4$ structure, a theoretical calculation of lattice expansion effects with changing

Table 1: Space group, Pearson symbol lattice parameters and heats of formation for $CeSiO_4$ and $LaSiO_4$ structures

Structure	Pearson symbol	Space group	a (Å)	b (Å)	c (Å)	ΔH_f (eV\atom)
$CeSiO_4$ (this study)	tl24	141/AMDZ	6.9564	6.9564	6.1953	-2.0740
$CeSiO_4$ (Kamal *et al.,* 2019)	tl24	141/AMDZ	7.0100	7.0100	6.9100	
$LaSiO_4$	mP24	P2_1/c	6.4700	7.0700	8.2399	-1.9500

Table 3: Calculated bulk (B), shear (G) and Young's (E) moduli values as well as the Poisson and Pugh ratios of t-CeSiO$_4$ and m-LaSiO$_4$ at 0 K.

Elastic modulus (GPa)	t-CeSiO$_4$		m-LaSiO$_4$
	This study	Exp. (Kamal *et al.,* 2019)	
B^v	151.38	150.67	108.57
G^v	69.43	64.60	46.25
E^v	180.68	169.57	121.50
Poisson's ratio	0.30		0.31
Pugh's ratio (B/G)	2.18		2.35

temperature was undertaken, with results illustrated in Figure 1. Figure 1 (a) shows that *a* and *b* lattice parameters increase linearly while c lattice parameter decreases (similarly linear) as the temperature is increased. This behaviour suggests that the structure t-CeSiO$_4$ is constructing along the *c* direction. An increase in *b* parameter behaviour shows that it expands linearly to the temperature of ± 2250 K after which elongation is halted, suggesting that there is no further expansion above the melting point (2273 K).
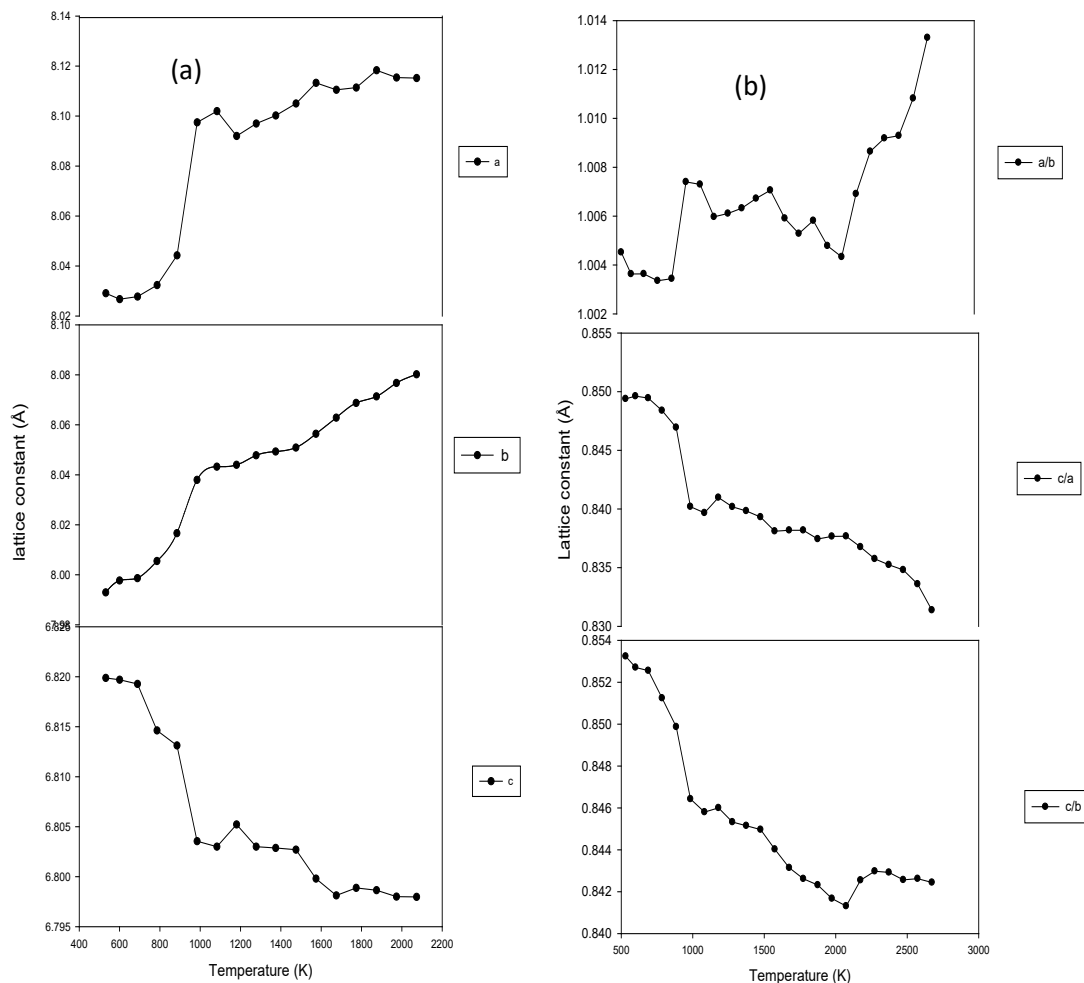
Note that lattice ratios (*a/b*, *c/a* and *c/b*) as shown in Figure 1 (b) are applied to determine the phase transformation temperature as a function of significant lattice parameter change. It is noted that the *a/b* ratio is approximately linear to the temperature of 2250 K, before a deviation is noted. This inflection which corresponds to the experimental melting point temperature of t-CeSiO$_4$ (2273 K) (Hikichi *et al.,* 1997) and is not ascribed to a structural transformational rearrangement but rather an artifact of melting. The *c/a* and *c/b* ratios display a similar linearity with ratios for both until the system approaches melting point and melting deviations are observed. Note that there is no temperature induced transformational phase changed observed in the t-CeSiO$_4$ structure.

4. Conclusion

The first-principle calculations were used to study the equilibrium lattice parameters, heats of formation and elastic properties of t-CeSiO$_4$ and m-LaSiO$_4$. The calculated lattice parameters for t-CeSiO$_4$ were found to be in good agreement with experimental values (within 3 % error) which implies a sufficient m-LaSiO$_4$ of the model system. From calculated elastic constants, it was found that the tetragonal CeSiO$_4$ structure is more stable on a macroscale) than the monoclinic m-LaSiO$_4$ analogue at 0 K, because it has a higher elastic shear modulus (C').

In order to compare and evaluate the hardness and ductility of the candidate structures, bulk, shear and Young's moduli and the Poisson ratio were of each candidate compound was calculated. It was noted that these theoretical values were in good agreement

Figure 1: (a) The effect of temperature on a, b and c lattice (b) on a/b, c/a and c/b ratio parameters of t- CeSiO$_4$.

with those noted from experimental results in literature (e.g within 5 % error for t-CeSiO$_4$). From these results in could be theoretically determined that both t-CeSiO$_4$ and m-LaSiO$_4$ are considered ductile in nature, substantiating what is observed with real-world macroscopic samples.

The high temperature phase evaluation of monazite was performed using LAMMPS code. It was shown that the t-CeSiO$_4$ structure expand along *a* and *b* lattice parameters and contracts along *the c* lattice parameter with an increase in temperature implying a structure that is constructed along the *c* direction. In addition, the lattice ratios *a/b*, *c/a* and *c/b* were compared in an attempt to determine if the structure undergoes a crystallographic phase transition before melting. The linearity of these ratios below a temperature of 2200 K would suggest that the monoclinic conformation remains intact until melting. The trends in these properties show that, when they are modified in a specific manner (for example, by high-temperature cracking), better results can be obtained regarding the liberation of cations from the material.

Acknowledgments

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