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The "bimodal effect" of the bulk modulus of rare-earth titanate pyrochlore

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ABSTRACT

First-principles calculations have been carried out to study the bulk modulus, the lattice parameters and the bond length of $RE_2Ti_2O_7$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) pyrochlores. The relationship of the bulk modulus and the bond length of $RE_2Ti_2O_7$ have been analyzed qualitatively. Both the bulk modulus and the $\langle RE\text{-}O_{48f}\rangle$ bond present the "bimodal effect" and $\langle RE\text{-}O_{48f}\rangle$ bond may have a significant effect on the bulk modulus.

1. Introduction

Pyrochlore-structured compounds with the form, $A_2B_2O_7$, have been the subject of extensive research due to their broad range of physical, chemical, magnetic, and electrical properties. This leads to significant potential for their use in a wide range of technical applications [1–3]. In particular, the bulk modulus is one of the most important physical parameters that characterize the mechanical property of materials. The bulk modulus has been found to correlate well with strength and hardness in many materials [4–6]. It is an extremely useful capability to predict the bulk modulus of crystalline materials by using density functional theory, since synthesis and measurement of some rare-earth titanate pyrochlores can be difficult to perform experimentally.

The nature of the chemical bonds can have an impact on macroscopic properties in pyrochlores. The radiation tolerance of pyrochlores has been correlated with the nature of the chemical bond in previous studies [7,8]. However, the relationship of the bulk modulus and the bond length in the rare-earth titanate pyrochlore has not been investigated. In this letter, the bulk modulus and some structural properties of the rare-earth titanate pyrochlore ($RE_2Ti_2O_7$) compounds were calculated by the density functional theory. The connection between the bulk modulus and the bond length of $\langle RE\text{-}O_{48f}\rangle$ (see Fig. 3) has been discussed. Meanwhile, a "bimodal effect" which means certain properties of lanthanide elements and compounds will not change linearly with the increase of atomic number of lanthanides but present two peaks or two valleys in Eu and Yb positions, is also clearly obtained in titanate pyrochlores. The successive change law of lanthanide elements and it's compounds have been investigated by Smith [9], Nugent [10] and Wen and Shao [23]. Similarly, the chemical and physical properties of these compounds have been observed unusual in Eu and Yb position. Because of this, the results of the present work are persuasive and easier to understand. However, the "bimodal effect" has not been observed in the rare-earth stannate pyrochlore and zirconate pyrochlore by Feng et al. [2,11]. In further study, a systematic in-depth analysis will be carried out to investigate the "bimodal effect" in rare-earth stannate and zirconate pyrochlore structure.

2. Computational details

All the calculations are performed with the Vienna Ab Initio Simulation Package (VASP) [12]. The interaction between ions and electrons is described using the projector augmented wave (PAW) method [13]. The exchange correlation interaction is described by PW91 functional [14]. f-Electrons of lanthanide elements in titanate pyrochlores are kept frozen in the core [7]. The lattice parameter and internal atomic positions of all structures are fully relaxed using a conjugate gradient scheme. The plane-wave energy cutoff is set to 550 eV, and a *k*-point grid of $4 \times 4 \times 4$ is used for Brillouin zone integration of the 22-atom primitive unit cell with spin polarized effects taken into account.

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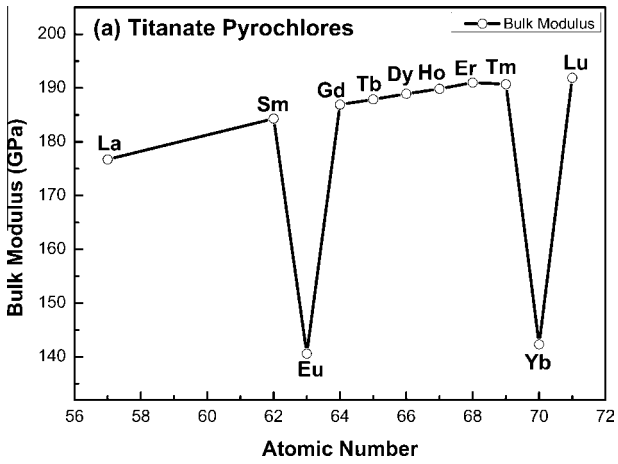

Fig. 1. Variation of the bulk modulus with the atomic number of RE for $RE_2Ti_2O_7$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).

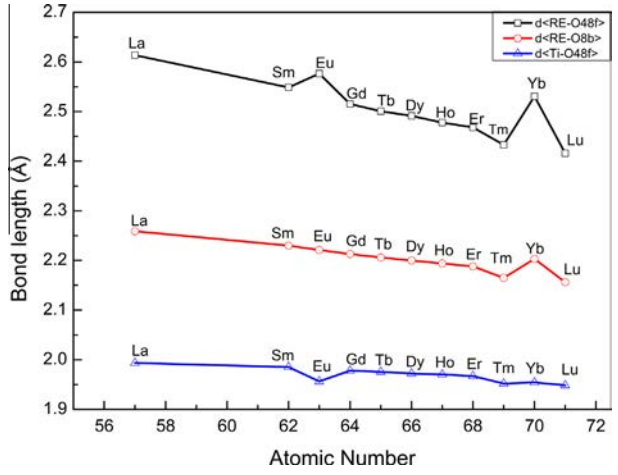

Fig. 2. Variation of the bond length with the atomic number of RE for $RE_2Ti_2O_7$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).

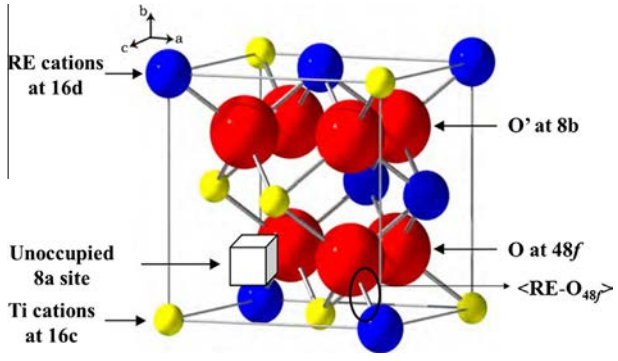

Fig. 3. Schematic view of one eighth of a unit cell of the pyrochlore structure. The RE and Ti metal cations occupy the 16d and 16c sites, respectively, and the oxygens of O and O′ are in the 48f and 8b positions, respectively. The missing oxygen are in the unoccupied 8a site.

The ionic relaxation is performed until the force is less than 0.001 eV/Å, and the electronic energies are converged to at least 1×10^{-5} eV/atom.

The elastic constants of the rare-earth titanate pyrochlores can be obtained by calculating second derivatives of the energy density $U(\delta)$ (which is defined as total energy per volume) as a function of properly chosen lattice distortions δ building up the strain. For a cubic structure, the independent elastic constants C_{11}, C_{12}, C_{44} can be obtained through volume compression and the tetragonal and trigonal strains, which are given by [15]:

$$\epsilon_{\text{comp}} = \frac{1}{3}\begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{pmatrix}, \epsilon_{\text{tetr}} = \frac{1}{2}\begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix}, \epsilon_{\text{trig}} = \begin{pmatrix} \delta^2 & \delta & \delta \\ \delta & \delta^2 & \delta \\ \delta & \delta & \delta^2 \end{pmatrix}.$$

The strain ϵ_{comp} describes volume compression, and ϵ_{tetr} and ϵ_{trig} refer to anisotropic tetragonal and trigonal lattice distortions, respectively. The elastic constants (or linear combinations of them) are the calculated from the energy by [15]:

$$\frac{\partial^2 U(\epsilon_{\text{comp}})}{\partial \delta^2} = B.$$

3. Results and discussion

To our best knowledge, except the theoretical value of the bulk modulus of $Gd_2Ti_2O_7$ [16], no experimental and theoretical data are available for the bulk modulus of the titanate pyrochlores studied in this work. It has to be considered that the values presented in Table 1 were obtained at $T = 0$ K. The bulk modulus of $RE_2Ti_2O_7$ shows an approximate linear relation with the increasing the atomic number of RE except for that of $Eu_2Ti_2O_7$ and $Yb_2Ti_2O_7$ (as shown in Fig. 1).

Electron configurations of the rare earth in titanate pyrochlores are list in Table 1 [17]. Changes in the electronic configuration of the rare earth atoms have an effect on the length of bond and thus affect the bulk modulus of titanate pyrochlores. It can be seen that all the lanthanide elements, except Eu and Yb, have one 5d electron and two 6s electrons. This means that electrons available for bonding in Eu and Yb are less than other lanthanide elements in titanate pyrochlores, and the bond strength are weaker. Whether ionic bond, covalent bond or metallic bond, bond strength varies inversely to bond length [18]. So the $\langle RE\text{-}O_{48f}\rangle$ bonds length will not change linearly with the increase of atomic number of lanthanides but present two peaks in Eu and Yb positions.

Several works have suggested that the bond length should be taken into account to explain the variation of the bulk modulus of materials [4,19]. It has been known that the bulk modulus are proportional to k/d^n where d is the bond length and k, n are determined by the properties of materials [19,20]. To investigate the relationship between bulk modulus and the bond length, the lattice parameters and bond length of $RE_2Ti_2O_7$ are calculated and listed in Table 2, together with available experimental and theoretical results [16,21,22]. Variation of the bond length of

Table 1
Electron configurations of the rare earths.

Rare earth	Atomic number	Solid state		
		4f	5d	6s
La	57		1	2
Sm	62	5	1	2
Eu	63	7		2
Gd	64	7	1	2
Tb	65	8	1	2
Dy	66	9	1	2
Ho	67	10	1	2
Er	68	11	1	2
Tm	69	12	1	2
Yb	70	14		2
Lu	71	14	1	2

Table 2
Calculated lattice constant a_0 (Å), bond length d (Å) and bulk modulus B (GPa) for $RE_2Ti_2O_7$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) compared with available experimental and theoretical values.

$RE_2Ti_2O_7$		a_0 (Å)	$d_{\langle RE\text{-}O48f\rangle}$ (Å)	$d_{\langle RE\text{-}O8b\rangle}$ (Å)	$d_{\langle Ti\text{-}O48f\rangle}$ (Å)	B (GPa)
La	This work	10.434	2.614	2.259	1.994	176.72
Sm	This work	10.300	2.549	2.230	1.985	184.29
	Other cal. (Ref. [21])	10.304	2.549	2.231	1.986	
	Exp. (Ref. [22])	10.206	2.524	2.210	1.968	
Eu	This work	10.259	2.576	2.221	1.957	140.60
	Other cal. (Ref.[21])	10.266	2.533	2.223	1.983	
	Exp. (Ref. [22])	10.1943	2.523	2.207	1.965	
Gd	This work	10.221	2.515	2.213	1.978	186.91
	Other cal. (Ref. [21])	10.226	2.517	2.214	1.979	
	Exp. (Ref. [22])	10.186	2.524		1.961	
	Other cal. (Ref. [16])	10.23				186
Tb	This work	10.189	2.500	2.206	1.976	187.87
	Other cal. (Ref. [21])	10.193	2.503	2.207	1.976	
	Exp. (Ref. [22])	10.1589	2.505	2.199	1.963	
Dy	This work	10.162	2.491	2.200	1.972	188.91
	Other cal. (Ref.[21])	10.164	2.490	2.201	1.974	
	Exp. (Ref. [22])	10.124	2.503	2.192	1.953	
Ho	This work	10.133	2.478	2.194	1.971	189.83
	Other cal. (Ref. [21])	10.137	2.479	2.195	1.971	
	Exp. (Ref.[22])	10.1041	2.489	2.187	1.954	
Er	This work	10.107	2.468	2.188	1.967	191.00
	Other cal. (Ref. [21])	10.114	2.469	2.190	1.969	
	Exp. (Ref. [22])	10.0787	2.488	2.182	1.946	
Tm	This work	10.000	2.433	2.165	1.953	190.69
	Other cal. (Ref.[21])	10.087	2.457	2.184	1.967	
	Exp. (Ref. [22])	10.0638	2.474	2.179	1.950	
Yb	This work	10.177	2.531	2.203	1.955	142.32
	Exp. (Ref. [22])	10.0325	2.503	2.192	1.953	
Lu	This work	9.959	2.416	2.156	1.949	191.89
	Other cal. (Ref. [21])	10.037	2.437	2.173	1.963	
	Exp. (Ref. [22])	10.0172	2.459	2.169	1.943	

$RE_2Ti_2O_7$ as a function of the atomic number of RE are shown in Fig. 2. It is found that the $\langle RE\text{-}O_{48f}\rangle$ bonds length presents the opposition direction of the bulk modulus, which are in good agreement with the empirical formula $B \propto k/d^n$. The bulk modulus will be affected by all kinds of chemical bond in $RE_2Ti_2O_7$. It is noticeable that the $\langle RE\text{-}O_{48f}\rangle$ bonds in $RE_2Ti_2O_7$pyrochlores may play a dominant role in determining the value of the bulk modulus. These are preliminary findings, and further research is needed to determine the value of k and n. The relationship between the bond length of all kinds of chemical bond and the bulk modulus in $RE_2Ti_2O_7$ should be investigated to decide the possible values of k and n in further research.

4. Conclusion

In summary, the bulk modulus, the lattice parameters and the bond length of $RE_2Ti_2O_7$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) pyrochlores have been investigated by the density functional theory (DFT). The results are compared with available experimental data and theoretical predictions. The bulk modulus of $RE_2Ti_2O_7$ do not grows linearly with the increasing atomic number of RE but a valley appears in $Eu_2Ti_2O_7$ and $Yb_2Ti_2O_7$ locations. However, the $\langle RE\text{-}O_{48f}\rangle$ bonds length shows an obviously opposite trend, which suggests that the $\langle RE\text{-}O_{48f}\rangle$ bonds in $RE_2Ti_2O_7$ pyrochlores may play a dominant role in determining the value of the bulk modulus.

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