Ab initio investigation of phase stability of $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ under high pressure

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(Received 30 November 2009; published 31 December 2009)

The phase stabilities of $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ under high pressure were investigated by *ab initio* methods. Pyrochlore-structured $Y_2Ti_2O_7$ and defect-fluorite $Y_2Zr_2O_7$ exhibit different responses to high pressure. Both the defect-fluorite and defect-cotunnite structures are energetically more stable at high pressure in $Y_2Ti_2O_7$, but comparison with experimental results suggest that only the transformation to the defect-fluorite structure is kinetically favored. For $Y_2Zr_2O_7$, the defect-fluorite phase should undergo a structural transformation to the defect-cotunnite state under high pressure.

The stability of pyrochlore-structured materials under extreme condition (i.e., irradiation, high temperature, and high pressure) is of fundamental interest in many fields, such as solid-state physics, material science, and nuclear engineering. For example, some zirconate pyrochlores, such as $Y_2Zr_2O_7$, $La_2Zr_2O_7$, and $Nd_2Zr_2O_7$ that are considered for possible applications in magnetohydrodynamic power generation, must withstand very severe environments.[1] Studies of pyrochlores under extreme condition not only develop basic insights into the effects on their structures and properties but also can lead to structural modification or the synthesis of new structures, as shown recently.[2–4]

Radiation-induced disordering or amorphization in pyrochlores has long been of interest, owing to the potential use of some pyrochlores as host matrices for the immobilization of actinides.[5] The structural phase transition from ordered pyrochlore to disordered defect states or amorphous structures can be induced not only by self-radiation from actinide decay[6] or external ion irradiation[7] but also by subjecting the pyrochlore compounds to high pressure.[2] High-pressure materials research has been revolutionized in the past few years due to technological breakthroughs. Also, the application of high pressure has revealed exciting manipulation of the properties of solids.[3,8] The structural stability of pyrochlores under high pressure has attracted growing experimental interest in recent years.[2,9–20] It appears that some pyrochlores show similar behavior under high-pressure and irradiation conditions. For example, the high-pressure phases of $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ are amorphous and disordered defect-fluorite structures, respectively,[2,13] similar to the case under irradiation.[7,21,22] Other pyrochlores, such as $Y_2Ti_2O_7$, exhibit different responses to high pressure and irradiation.[13,21] Another interesting phenomenon is that under high pressure a new cotunnitelike phase was observed for both defect-fluorites $Er_2Zr_2O_7$ and $Ho_2Zr_2O_7$.[10] Nevertheless, no theoretical evidence or prediction of the phase stability of pyrochlores under high pressure has been provided so far, one reason for this may be the fact that it is difficult to characterize defect structures in pyrochlores.

Ordered pyrochlores, $A_2B_2O_7$, are of *Fd*-3*m* space group,[23–25] in which the *A* and *B* cations occupy 16*d* and 16*c* sites, respectively. In the defect-fluorite (space group: *Fm*-3*m*) structures, the cations and anions are randomly distributed on 4*a* and 8*c* positions, respectively, with one eighth of the anion positions vacant. Both cations and anions are randomly distributed on 4*c* positions in the

defect-cotunnite[10] (space group: *Pnma*) structures and one eighth of the anions are missing. A defect cluster consisting of both an oxygen Frenkel and cation antisite defects in nearest-neighbor positions,[26,27] a random inversion of half the cations of each type with no oxygen-atom disorder,[28] and a special quasirandom structure (SQS) approach[29] have been employed to simulate the defect-fluorite structures. In the present study, a randomization method was employed to create the defect-fluorite and defect-cotunnite structures in $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$. The defect-fluorite structures obtained by this method are more stable than those obtained from other methods. Using these defect structures, we performed *ab initio* calculations on $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ to explore their phase stability under high pressure, with pyrochlore and amorphous states also considered. These two compounds were chosen for study because $Y_2Ti_2O_7$ has the stable pyrochlore structure, while $Y_2Zr_2O_7$ has the defect-fluorite structure under ambient conditions.

All the calculations were performed with the VASP code.[30] The interactions between ions and electrons were described using the projector augmented wave method,[31] and the exchange-correlation functional was determined within the generalized gradient approximation parametrized by Perdew and Wang. This method has proved to be an improvement over localized density approximation results in the description of energies of systems because of consideration of the gradient of charge density when describing the exchange-correlation energy.[32] To study the phase stability of these systems under high pressure, we calculated and compared the enthalpies of four different phases with pressures ranged from 0 to 80 GPa: (1) ideal pyrochlore (P type), (2) defect-fluorite (F type), (3) defect-cotunnite (C type), and (4) amorphous state (A type). The simulation cell for each system consists of 88 atoms. A randomization method, in which more than 80 random configurations consisting of random distribution of cations and anions on their respective sublattices were optimized completely, was used to characterize F-type and C-type structures, and only the most stable ones are discussed. The F-type structures obtained are 8.13 and 5.76 eV more stable than those from SQS method for $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$, respectively. The A-type model was constructed by an *ab initio* molecular-dynamics method;[33] in this case, the initial P-type configuration was melted at 4500 K for 10 ps and then quenched to 0 K. The amorphous structure obtained by this method was subsequently relaxed completely by *ab initio* methods. All the *ab initio* calculations
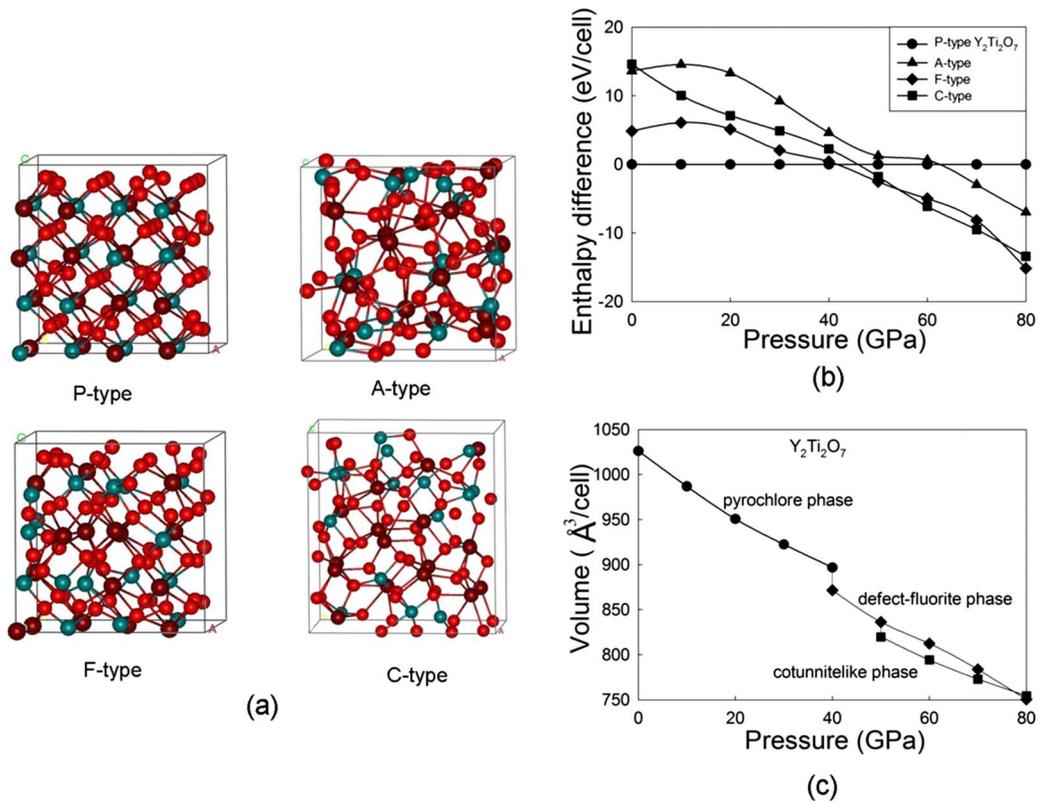
FIG. 1. (Color online) (a) Schematic view of the optimized configurations for the P-, A-, F-, and C-type structures of $Y_2Ti_2O_7$. (b) Variation in the enthalpy difference between all the considered phases and P-type $Y_2Ti_2O_7$ as a function of pressure. (c) Variation in volume of P-, F-, and C-type structures of $Y_2Ti_2O_7$ with pressure.

were carried out with a $2 \times 2 \times 2$ k-point sampling in reciprocal space and with a cut-off energy of 450 eV for the plane-wave basis set. The optimized structural parameters and calculated disordering energy for $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ in P-type states are comparable with available experiments and theoretical calculations.[21,34]

The optimized configurations for the four phases of $Y_2Ti_2O_7$ under ambient condition are illustrated in Fig. 1(a). Significant structural distortions with lowered symmetry, as compared with P-type structure, are observed for both defect states, especially for the C-type phase. For A-type $Y_2Ti_2O_7$, local chemical bonding is still observed. The optimized structural parameters are $a=10.09$ Å, $x=0.3302$ for P type, $a=10.18$ Å for F type, and $a=11.6$ Å, $b=6.76$ Å, $c=12.7$ Å for C-type $Y_2Ti_2O_7$. Experimental measurements of $a=10.1$ Å, $x=0.330$ have been reported for P-type $Y_2Ti_2O_7$.[21] Figure 1(b) shows the variation in the enthalpy difference of all the phases relative to P-type $Y_2Ti_2O_7$ with pressure. As can be seen from the figure, a phase transformation for $Y_2Ti_2O_7$ from P type to F type becomes energetically favorable at ~40 GPa and from P type to C type at ~46 GPa. It is noted that the enthalpy difference between the F- and C-type structures under high pressure is small, and the high-pressure state should be a coexistence of both structures, unless the transformation to one structure is kinetically limited. Experimental studies[14] have shown that the high-pressure phase for $Y_2Ti_2O_7$ consists primarily of the defect-fluorite structure with some amounts of amorphous phase. This suggests that the transformation to the equally energeti-

cally stable C-type structure may be kinetically limited by higher energy pathways, which is not surprising given the need to randomize anions and cations on the same lattice site. As a result, the high-pressure transformation of the $Y_2Ti_2O_7$ P-type to the F-type structure dominates. As pressure increases to about 62 GPa, the amorphous state becomes energetically stable. This could explain the presence of some amorphous phase observed experimentally under high pressures, particularly if the transformation barrier to the amorphous state is comparable to that for the most stable F-type structure. Several less stable F-type and C-type structures were also investigated for comparison. The results show that the P-type structure will not transform to such less stable F-type structures. In contrast, the less stable C-type structures show structural responses similar to that for the most stable C-type structure. The pressure dependence of the unit-cell volume for the P-type and defect structures is illustrated in Fig. 1(c). There is a 2.8% and 5.7% volume reduction as the P-type→F-type and P-type→C-type phase transformations occur. It should be pointed out that since the defect structures are obtained from the randomization method, it is possible that more stable defect structures may exist, which could lead to different phase-transformation pressures. However, the high-pressure phase stabilities and transformation trends predicted from our calculations are reasonably consistent with experiment.

Unlike $Y_2Ti_2O_7$, the defect-fluorite structure for $Y_2Zr_2O_7$ is 2.67 eV more stable than the P-type structure under ambient conditions, which is consistent with both experimental
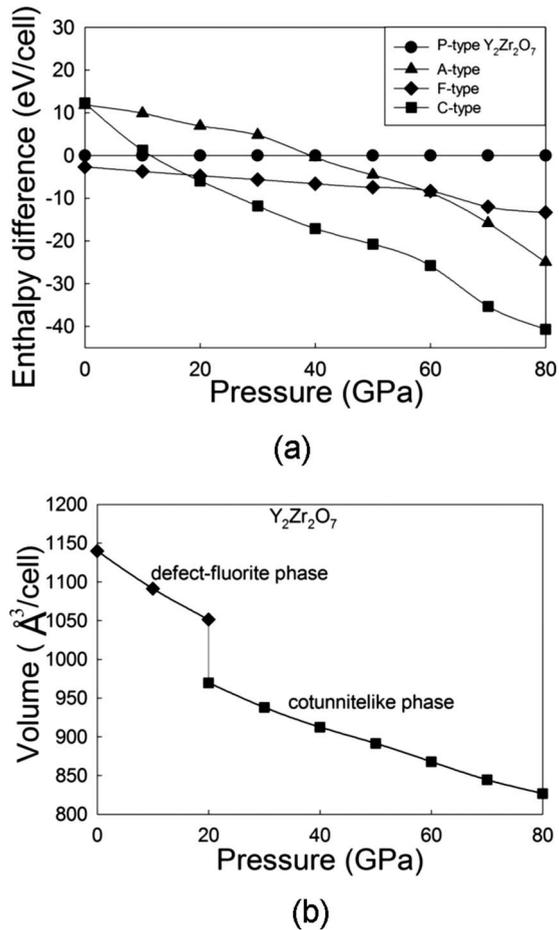
FIG. 2. (a) Variation in the enthalpy difference between all the considered phases and P-type states as a function of pressure. (b) Variation in volume of P-, F-, and C-type structures of $Y_2Zr_2O_7$ with pressure.

FIG. 3. (Color online) Pair-correlation function for P type and F type (a) $Y_2Ti_2O_7$ and (b) $Y_2Zr_2O_7$ under ambient condition.

observations and other theoretical predictions.[27,35–39] The optimized structural parameters are $a=10.499$ Å, $x=0.3417$ for P type, $a=10.44$ Å for F type, and $a=11.66$ Å, $b=6.78$ Å, $c=13.18$ Å for C type. Figure 2(a) shows the enthalpy difference between all the considered phases and the pyrochlore state as a function of pressure. At ~18 GPa a phase transformation from F type to C type becomes energetically favorable, and the C-type structure remains very stable under higher pressure. Similar to the case of $Y_2Ti_2O_7$, the defect-cotunnite phase for $Y_2Zr_2O_7$ has much higher symmetry with only small distortions under high pressure; however, it is less stable than the amorphous state under ambient conditions. As the pressure increases to ~60 GPa, the amorphous phase becomes energetically favorable. Unless kinetically limited, our calculations show that the structural response of defect-fluorite $Y_2Zr_2O_7$ to pressure should be similar to that of defect-fluorite $Er_2Zr_2O_7$ and $Ho_2Zr_2O_7$, which were found to be unstable and undergo a sluggish (kinetically slow) defect-fluorite to cotunnitelike phase transformations at ~22 GPa for $Er_2Zr_2O_7$ and ~30 GPa for $Ho_2Zr_2O_7$.[10] Hopefully, this will be validated by future experimental measurements. The high-pressure responses of some less stable F-type $Y_2Zr_2O_7$ were also investigated for comparison, and the results show
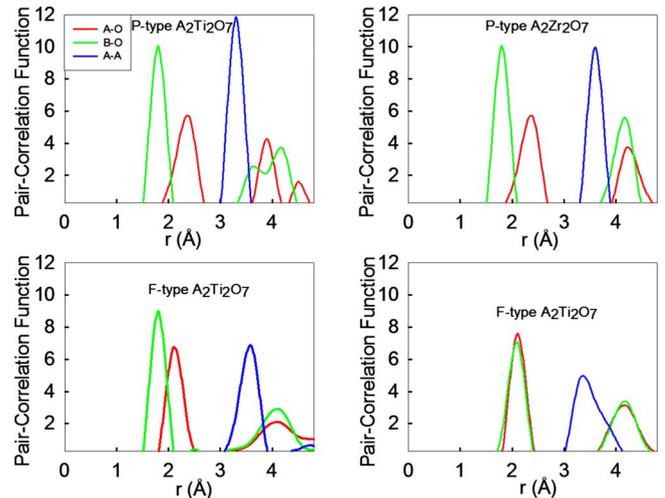
that the F-type to C-type phase transition is observed in all the cases; whereas the transition pressures are relatively smaller. Figure 2(b) presents the pressure dependence of the unit-cell volume for the F- and C-type structures of $Y_2Zr_2O_7$, in which the volume of the unit cell decreases by approximately 14.3% during the F-→C-type phase transition at ~18 GPa.

For $A_2B_2O_7$ compounds, it has been suggested that the propensity for forming the defect-fluorite structure generally depends on the cation radii[40] or the iconicity of the material.[41] Our calculations show that other factors, including symmetry and bonding interactions, should also be taken into account. In the present study, it is shown that under ambient condition both cations in F-type $Y_2Zr_2O_7$ are primarily sevenfold coordinated to oxygen anions; whereas F-type $Y_2Ti_2O_7$ exhibits significant structural distortion, and Y^{3+} and Ti^{4+} in F-type $Y_2Ti_2O_7$ have six, seven, or eight nearest-neighbor anions. This results in the high symmetry of F-type $Y_2Zr_2O_7$ and lower symmetry of F-type $Y_2Ti_2O_7$. Figure 3 shows the pair-correlation function (PCF) for all the cation-anion and *A*-*A* cation pairs for P-type and F-type $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ under ambient conditions. The PCF for *B*-*B* cation and *A*-*B* cation pairs is, on average, similar to *A*-*A* cation pair. Also, the PCF distribution for anion-anion pairs provides little information and is not presented in the figure. One striking feature of this plot is that the first peak of the PCF for the cation-cation pairs appears at 3.3 Å for P-type $Y_2Ti_2O_7$ and F-type $Y_2Zr_2O_7$, while for the F-type $Y_2Ti_2O_7$ and P-type $Y_2Zr_2O_7$, the first peak generally appears at relatively larger distance (about 3.6 Å). This suggests that stronger cation-cation interactions exist for both P-type $Y_2Ti_2O_7$ and F-type $Y_2Zr_2O_7$. Direct overlap of cation *d*-electron wave functions, as observed in several oxides containing transition elements,[42] may be responsible for the cation-cation interaction.

Fitting the pressure-volume data in Fig. 1(c) to the Murnaghan equation of state yields bulk modulus values of 192, 80, and 92 GPa for P-, F-, and C-type $Y_2Ti_2O_7$, respectively. For $Y_2Zr_2O_7$, the bulk moduli of F- and C-type structures are

determined to be 156 and 116 GPa, respectively. It is suggested that under high pressure both compounds are likely to transform to the phases with larger compressibility. The reason the F-type structure is stable for $Y_2Ti_2O_7$, but not for $Y_2Zr_2O_7$, under high pressure may be due to the much larger compressibility of the F-type $Y_2Ti_2O_7$. Another observation is that the average cation-anion bonding distance increases from 2.11 to 2.33 Å for the P-type to F-type transformation in $Y_2Ti_2O_7$ at ~40 GPa and from 2.2 to 2.4 Å for F-type to C-type transformation in $Y_2Zr_2O_7$ at ~18 GPa. Experimentally, the increased cation-anion bonding distance after the phase transformation has been attributed to an increase in the coordination number.[10] Figure 4 shows the density of state distribution at high pressure. A significant hybridization is observed between O $2p$, Y $3d$, and Ti $3d$ or Zr $4d$ orbitals below the Fermi level. This interaction occurs over a wider energy range for the high-pressure phases. It is also observed that the band gap decreases significantly after phase transition, which is deduced from the band gap value of 2.97 and 1.40 for the P-type and F-type $Y_2Ti_2O_7$, and 2.73 and 1.98 eV for F-type and C-type $Y_2Zr_2O_7$. These results indicted that the phase transformation under high pressure is accompanied by enhanced compressibility, increased average cation-anion bonding distances and decreased band gap.

In summary, we provide a theoretical basis for the experimental observation of a pyrochlore to defect-fluorite phase transformation in $Y_2Ti_2O_7$ and predict the response behavior of defect-fluorite $Y_2Zr_2O_7$ to high pressure. A coexistence of both defect-fluorite and defect-cotunnite structures under high pressure (>40 GPa) is predicted for $Y_2Ti_2O_7$; however, comparisons with experimental results indicate that the transformation to the defect-cotunnite structure may be kinetically limited. While defect-fluorite $Y_2Ti_2O_7$ exhibits high stability under high pressure, defect-fluorite $Y_2Zr_2O_7$ is predicted to be less stable than the defect-cotunnite structure at
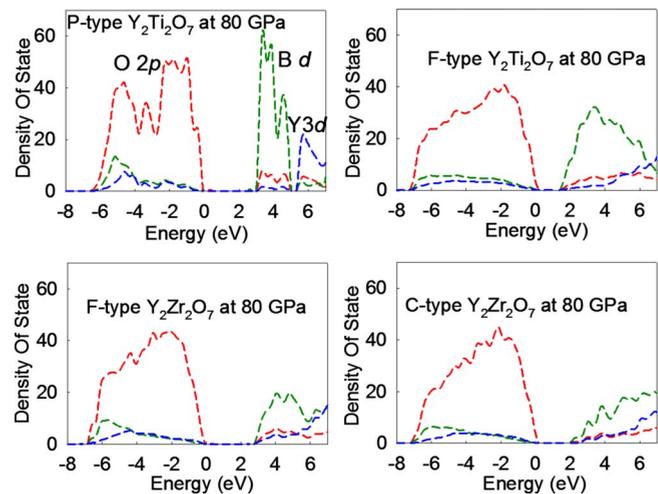

FIG. 4. (Color online) Density of state distribution for $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$ at high pressure.

~18 GPa. These phase transformations are accompanied by enhanced compressibility, increased average cation-anion bonding distance and decreased band gap.

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[1] R. A. Chapman *et al.*, J. Phys. D **3**, 307 (1970).
[2] F. X. Zhang *et al.*, Phys. Rev. Lett. **100**, 045503 (2008).
[3] M. Lang *et al.*, Nature Mater. **8**, 793 (2009).
[4] A. Chartier *et al.*, Phys. Rev. Lett. **102**, 155503 (2009).
[5] R. C. Ewing *et al.*, J. Appl. Phys. **95**, 5949 (2004).
[6] W. J. Weber *et al.*, J. Nucl. Mater. **138**, 196 (1986).
[7] S. X. Wang *et al.*, J. Mater. Res. **14**, 4470 (1999).
[8] Y. S. Yao *et al.*, Phys. Rev. Lett. **103**, 055503 (2009).
[9] R. S. Kumar *et al.*, Phys. Status Solidi B **244**, 266 (2007).
[10] F. X. Zhang *et al.*, Appl. Phys. Lett. **92**, 011909 (2008).
[11] F. X. Zhang *et al.*, Phys. Rev. B **76**, 214104 (2007).
[12] F. X. Zhang *et al.*, Chem. Phys. Lett. **441**, 216 (2007).
[13] F. X. Zhang and S. K. Saxena, Chem. Phys. Lett. **413**, 248 (2005).
[14] F. X. Zhang *et al.*, Mater. Lett. **60**, 2773 (2006).
[15] N. R. S. Kumar *et al.*, Solid State Commun. **147**, 357 (2008).
[16] R. S. Kumar *et al.*, Appl. Phys. Lett. **88**, 031903 (2006).
[17] S. Saha *et al.*, Phys. Rev. B **79**, 134112 (2009).
[18] S. Saha *et al.*, Phys. Rev. B **78**, 214102 (2008).
[19] D. Y. Kim *et al.*, J. Phys. Chem. Solids **69**, 2245 (2008).
[20] N. Takeshita *et al.*, J. Phys. Soc. Jpn. **76**, 063707 (2007).
[21] J. Lian *et al.*, Phys. Rev. B **68**, 134107 (2003).
[22] J. Lian *et al.*, Phys. Rev. B **66**, 054108 (2002).
[23] N. Li *et al.*, J. Appl. Phys. **102**, 063704 (2007).
[24] H. Y. Xiao *et al.*, J. Phys.: Condens. Matter **19**, 346203 (2007).
[25] H. Y. Xiao *et al.*, J. Appl. Phys. **104**, 073503 (2008).
[26] P. J. Wilde and C. R. A. Catlow, Solid State Ionics **112**, 173 (1998).
[27] M. J. D. Rushton *et al.*, J. Mater. Res. **19**, 1603 (2004).
[28] A. Chartier *et al.*, Phys. Rev. Lett. **94**, 025505 (2005).
[29] C. Jiang *et al.*, Phys. Rev. B **79**, 104203 (2009).
[30] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[31] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[32] Y. M. Juan *et al.*, Phys. Rev. B **51**, 9521 (1995).
[33] F. Gao *et al.*, Phys. Rev. Lett. **103**, 027405 (2009).
[34] W. R. Panero *et al.*, Phys. Rev. B **70**, 054110 (2004).
[35] K. Shimamura *et al.*, Int. J. Thermophys. **28**, 1074 (2007).
[36] Y. Tabira *et al.*, J. Solid State Chem. **294**, 99 (2001).
[37] H. Yamamura *et al.*, Solid State Ionics **158**, 359 (2003).
[38] W. E. Klee and G. Weitz, J. Inorg. Nucl. Chem. **31**, 2367 (1969).
[39] M. T. Vandenborre *et al.*, Spectrochim. Acta, Part A **37**, 113 (1981).
[40] K. E. Sickafus *et al.*, Science **289**, 748 (2000).
[41] K. Trachenko, J. Phys.: Condens. Matter **16**, R1491 (2004).
[42] J. B. Goodenough, Phys. Rev. **117**, 1442 (1960).