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Effects of A^{3+} cations on hydration in $A_2M_3O_{12}$ family materials: A first-principles study

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ABSTRACT

By using first-principles calculations, we have systematically investigated the hydration in $A_2M_3O_{12}$ (A = Y, Er, Yb, Lu, In, Sc; M = Mo, W) family materials, focusing on the role of the ionic radius and electronegativity of A^{3+} cations on the hydration of the materials. Our calculations showed that O end of the inserted H_2O prefers to bind to A^{3+} or M^{6+} cations depending on the ionic radius and electronegativity of A^{3+} cations. As the radius of A^{3+} cations decreasing from $R(Y^{3+}) = 0.90$ to $R(Sc^{3+}) = 0.75$ Å, the binding site of H_2O is shifted from the position near the A^{3+} cations to that between the A^{3+} and the M^{6+} cations, finally to the position between the two M^{6+} cations. The binding energy is generally decreased as R decreasing (exception for A = Sc). Meanwhile, in all the cases two H of H_2O tend to point to the nearby bridge O atoms sharing by AO_6 octahedra and MO_4 tetrahedra, and form hydrogen bonds, which play a key role in the binding between H_2O and the materials. It was also found that the tungstates generally exhibit weak hygroscopicity comparing to the corresponding molybdates. Our results revealed the relationship between the hygroscopicity and the ionic radius of the A^{3+} cations, and provided a theoretical guidance in synthesis of $A_2M_3O_{12}$ family materials with weak hygroscopicity.

1. Introduction

The $A_2M_3O_{12}$ (A = Y, Er, Yb, Lu, In, Sc; M = Mo, W) family negative thermal expansion (NTE) compounds have attracted a lot of attention because of their great chemical flexibility, large temperature range for the NTE performance and anisotropic expansion for their orthorhombic structures [1–6]. Besides this, $A_2M_3O_{12}$ family material also have excellent performance in ionic conduction [7–11]. These remarkable features make these compounds potential constituents in composites to tailor the thermal expansion to a desired value with potential applications in optics, optoelectronics, and other fields. In recent years, more and more research focus on the mechanism of NTE or modulating the coefficient of thermal expansion (CTE) in different materials, such as oxide with framework structure, perovskite and anti-perovskite materials [12–21]. Recently, Lei Hu, et al. synthesized a near zero expansion material over a wide temperature range through co-doping of Ga and Fe in ScF_3 to modulate its CTE [22]. Chemical modifications have become main technique to control the thermal expansion [23].

The oxide materials with the framework structures, such as $A_2M_3O_{12}$ family materials, have a highly hygroscopicity which obstacle its NTE performance at room temperature [24–26]. It is found that $Y_2W_3O_{12}$ reversibly forms a tri-hydrate compounds, and cell volume of the hydrated pattern is 7% smaller than the un-hydrated cell volume [24,25]. Unlike $Y_2W_3O_{12}$, the hydration of ZrW_2O_8 does not occur at room temperature, but exposing it to water at higher temperature and pressure can cause insertion of water into the framework [26]. Sumithra et al. have reported that the rare earth molybdates and tungstates of $A_2M_3O_{12}$ family with an orthorhombic structure (A = Y, Er, Yb, Lu) are highly hygroscopic and exhibit NTE after complete removal of water molecules [27,28]. It is also found that presence of micro-channels in $Y_2Mo_3O_{12}$ are large enough to accommodate the H_2O molecules, and these H_2O molecules have a role in partial amorphization of $Y_2Mo_3O_{12}$ at room temperature [29]. To eliminate the hygroscopicity of $A_2M_3O_{12}$ family materials, many researches have been dedicated to synthesize materials by substituting different elements of A^{3+} cations [30–33]. Our theoretical study also indicated that $Y_2Mo_3O_{12}$ could absorb H_2O strongly with O of H_2O binding to the Y^{3+} cation and two H pointing to the nearby bridge O and forming hydrogen bonds. The absorption of H_2O molecule in $Y_2Mo_3O_{12}$ leads to the volume shrink of the unit cell, and the hydrogen bonds between the H_2O and $Y_2Mo_3O_{12}$ hinder the vibration modes which induced the NTE [34]. It was found that $A_2M_3O_{12}$ family materials with different ionic radius of A^{3+} cations have different extent in hygroscopicity in experiment [27,28]. However, a systematic

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theoretical studies about water absorption in the $A_2M_3O_{12}$ family materials have not been found. A relationship between the absorption properties of water and radius of A^{3+} cations is still obscure. In this paper, we studied H_2O absorption in the $A_2M_3O_{12}$ (A = Y, Er, Yb, Lu, In, Sc; M = Mo, W) family materials by using first-principles calculations. Our results revealed that the O of H_2O molecule (O@H_2O) binds to A^{3+} or M^{6+} cation depending on the ionic radius of A^{3+} cations and two H of H_2O molecule (H@H_2O) always form hydrogen bonds with the nearby bridge O atoms, which sharing by the "rigid units" of AO_6 octahedra and MO_4 tetrahedra. The hydrogen bonds enhance the binding between H_2O and the materials and play key role in the hydration of the materials.

The paper is organized as follows. Our calculation method and model systems are described in Section 2. In Section 3 absorption energy and optimized geometry of H_2O molecule absorption in $A_2M_3O_{12}$ (denoted as $H_2O@A_2M_3O_{12}$) have been studied, and the binding property and charge redistribution due to water absorption were analyzed, focusing on the effects of the ionic radius and electronegativity of A^{3+} cations on the geometry and binding property of water in the materials. In Section 4 some conclusions are given.

2. Methodology

The first-principles calculations are performed based on the density functional theory (DFT) with a generalized gradient approximation (GGA) in the form of PBE (Perdew–Burke–Ernzerhof) [35] implemented in the VASP [35–38] (Vienna *ab initio* Simulation Package) code, including van der Waals (vdW) interaction corrections in the form of DFT-D2 method of Grimme [39]. Valence electrons are treated explicitly and their interactions with ionic cores are described by PAW [40,41] (Projector Augmented Wave) pseudopotentials. The wave functions are expanded in a plane wave basis set with an energy cutoff of 500 eV. A k-point sampling of $2 \times 2 \times 2$ Monkhorst-Park grids [42] in the first Brillouin zone of the unit cell is used in the calculation. This is established by performing a convergence test using an even more dense k-point grids ($3 \times 3 \times 3$ k-point mesh), in which a very small total energy difference of 0.009 meV per atom is obtained compared to the result of the $2 \times 2 \times 2$ Monkhorst-Park grids. The reciprocal-space energy integration is performed by the Gaussian smearing method with a width of $\sigma = 0.02$ eV. The $H_2O@A_2M_3O_{12}$ system is modeled by having one H_2O molecule in a $1 \times 1 \times 1$ cuboid $A_2M_3O_{12}$ unit cell and with periodic boundary conditions. All atoms in the unit cell are allowed to relax until the forces on each atom are smaller than 0.01 eV/Å and the energy difference is smaller than 10^{-4} eV/atom. In our previous article [34], we have studied the volume shrink of unit cell of $Y_2Mo_3O_{12}$ during hydration, which can be interpreted the distance between the YO_6 octahedrons and MoO_4 tetrahedron shrinking due to the hydrogen bond between the H@H_2O and bridge O. Besides this, we also found that the volume shrink increased as the number of absorption H_2O increased. Therefore, in order to investigate the structural change due to water absorption, the shape and volume of unit cell have been relaxed based on the initial orthorhombic structure of the compounds.

3. Results and discussion

3.1. Structures of clean $A_2M_3O_{12}$

Before going to investigate the absorption of $H_2O@A_2M_3O_{12}$, we firstly optimized the structures of $A_2M_3O_{12}$ with space group of *Pbna* (No. 60). The primitive cell of $A_2M_3O_{12}$ has 68 atoms, which comprise of 12 MO_4 tetrahedra and 8 AO_6 octahedra, MO_4 tetrahedra connects with AO_6 octahedra by sharing O atom. The initial atomic structures of the molybdate and tungstate with different A^{3+} cations are constructed according to the coordinates of $Sc_2Mo_3O_{12}$ which were reported in previous experiment [6]. The calculated lattice parameters of the relaxed molybdates and tungstates structures with various elements A are listed in Table 1, and the available experimental values in literatures are also presented in the brackets for a comparison. It can be seen that for A = Y^{3+} cation the systems of molybdate and tungstates have the largest lattice constants, in agreement with the fact that the ionic radius of Y^{3+} cation is the largest one (see Table 3). We also found that the calculated lattice constants are reduced as the ionic radius of A or M decreased. Our calculated results are generally in line with the experimental measurements. We therefore concluded that our calculations gave a reliable description to the $A_2M_3O_{12}$ systems.

Table 1
Calculated lattice parameters in the studied compounds of $A_2M_3O_{12}$ family materials. Values in brackets are available experimental results.

	Molybdates			Tungstates		
	a (Å)	*b* (Å)	*c* (Å)	*a* (Å)	*b* (Å)	*c* (Å)
Y	10.05	10.18	13.93	10.11	10.21	14.23
	(9.93)	(10.02)	(13.87) [29]	(9.99)	(10.08)	(13.95) [46]
Er	9.74	9.88	13.63	9.79	9.94	13.62
	(9.92)	(10.03)	(13.85) [27]	(9.95)	(10.05)	(13.90) [47]
Yb	9.71	9.84	13.58	9.72	9.85	13.58
	(9.84)	(9.98)	(13.77) [27]	(9.89)	(9.97)	(13.81) [47]
Lu	9.65	9.79	13.50	9.79	9.91	13.50
	(9.83)	(9.92)	(13.70) [27]	(9.86)	(9.95)	(13.77) [4]
In	9.55	9.67	13.33	9.65	9.74	13.31
	(9.59)	(9.70)	(13.34) [48]	(9.61)	(9.71)	(13.38) [43]
Sc	9.59	9.68	13.28	9.49	9.58	13.15
	(9.56)	(9.65)	(13.24) [6]	(9.60)	(9.69)	(13.30) [4]

To study the bonding property in different tungstates and molybdates, we calculated the charge density distribution of different $A_2M_3O_{12}$ materials, and depicted the local charge density distributions of three representative molybdates and tungstates ($Y_2Mo_3O_{12}$, $Y_2W_3O_{12}$, $Yb_2Mo_3O_{12}$, $Yb_2W_3O_{12}$, $Sc_2Mo_3O_{12}$ and $Sc_2W_3O_{12}$) in Fig. 1.

As previous reported, A–O bond has ionic feature, while M–O bond prefers to be covalent feature [45] (see Fig. 1). As depicted in Fig. 1, the charge density at the middle points of Mo–O bond and W–O bond are 0.08, 0.06 e/A^3, respectively, which illustrates that the Mo-O bond in molybdates are more strong covalent nature than that of W–O bond in tungstates. This is because Mo being more easily to lose its electrons to the O atom than W (W has larger electronegativity than Mo). To certify this, we also calculated the Bader effective charge [49]. Using the Bader charge and the number of valence electrons, we calculated the average effective charge, $Q = Z_{\text{val}} - Q_{\text{Bader}}$, on every chemical species, where $Z_{\text{val}} = 11$, 9, 8, 9, 13, 11, 6, 6 and 6 e for Y, Er, Yb, Lu, In, Sc, Mo, W and O atoms, respectively. Our calculated results are listed below. From Table 2, we can see that O atoms obtain electron from A atoms and M atoms. Besides this, we also found that the O atoms obtain more electrons from W atoms than that from the Mo atoms in M–O bond, which resulted a weaker W–O covalent bond than Mo–O covalent bond. And this is agreement with the charge distribution which is shown in Fig. 1.

It is also found that the covalent nature of A–O bond enhanced from Y to Sc in the materials as the ionic radius decreased and electronegativity increased from Y to Sc. All these bond features and size of A^{3+} cations will affect the geometry and binding energy of H_2O absorption in the materials.

3.2. Absorption of H_2O in $A_2M_3O_{12}$ materials

In this section, we discussed H_2O absorption in the porous of $A_2M_3O_{12}$ family materials and checked the effect of A^{3+} cations