Phys Chem Minerals (2006) 33:545–552
DOI 10.1007/s00269-006-0100-3

ORIGINAL PAPER

Thorite versus huttonite: stability, electronic properties and X-ray emission spectra from first-principle calculations

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Received: 5 May 2006 / Accepted: 23 June 2006 / Published online: 2 August 2006

Abstract The structural, electronic properties and stability of thorium orthosilicate $ThSiO_4$ polymorphs: thorite and huttonite are investigated by means of the full-potential linearized augmented-plane-wave method with the generalized gradient approximation for the exchange-correlation potential (FLAPW-GGA). The forbidden gaps of thorite and huttonite are estimated at about 7.8 and 7.6 eV, respectively. It is found that Th5f states in $ThSiO_4$ partially overlap with occupied O2p bands. The data obtained showed that thorite is more stable than huttonite; in turn both $ThSiO_4$ polymorphs are unstable with respect to their constituent binary oxides (thorianite ThO_2 and α-quartz SiO_2) in agreement with the experiments. The theoretical shapes of X-ray emission (XES) (Si,O)Kα,β spectra for thorite, huttonite as well as for SiO_2 and ThO_2 are calculated and discussed. We show that the XES spectroscopy near the (Si,O)K edge may be very useful technique not only for detailed investigation of the bulk-electronic structure of Th silicates but also for the phase analysis of complex mineral samples containing these species.

Keywords Thorite · Huttonite · α-Quartz · Thorianite · Phase stability · Electronic structure · X-ray emission spectra · FLAPW-GGA

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Introduction

Thorite and huttonite (the polymorphs of thorium orthosilicate $ThSiO_4$) are members of the general ABO_4 mineral group (where A = Sc, Zr, Hf, lanthanides or actinides, and B = Si or P) and are of great interest in physics, chemistry and mineralogy. Thorite and huttonite occur widely in forms of accessory minerals, which belong to the basic commercial minerals of thorium. On the other hand, synthetic thorium orthosilicate belongs to few individual phases which can be obtained in ternary systems Th–X–O, where X are the IVa Group elements (Keller 1976). Today several routes are developed to synthesize $ThSiO_4$: via sol-gel approach (Vance 1986), solid-state synthesis (Vilmin et al. 1987; Ushakov et al. 1999), vapor-phase reaction (Kamegashira 1979) and some others (see Keller 1976; Mazeina et al. 2005 and references cited in them).

In spite of the fact that ABO_4 compounds are very attractive materials for practical use, as against zircon ($ZrSiO_4$) and hafnon ($HfSiO_4$) only limited information about the properties of $ThSiO_4$ polymorphs is available. Among them the structural and thermodynamic properties are the most investigated (see Keller 1976; Taylor and Ewing 1978; Wu and Farges 1999; Grover et al. 2005; Mazeina et al. 2005). Some attempts have been made recently to understand the radiation effects in $ThSiO_4$ for the development of radiation-resistant materials (Meldrum et al. 1998, 2000) and the crystalline-to-metamict transformation in the orthosilicates (Meldrum et al. 1999a). Additionally, optic and EPR parameters of Yb^{3+}, U^{4+}, Np^{4+} and Pu^{4+} ions as dopants introduced in $ThSiO_4$ matrix are studied (Lahalle et al. 1986; Malek and

Krupa 1986; Krupa and Carnall 1993; Dong et al. 2006).

Over the last years, significant achievements in the fundamental understanding of electronic, structural, optical properties and phase stability of some ABO_4 materials were provided by the results of electronic density-functional theory (DFT) based ab initio calculations (see, e.g., Rignanese et al. 2001; Terki et al. 2005a; Robertson et al. 2006). However, as far as we know, any data about electronic properties of $ThSiO_4$ polymorphs are absent.

In this paper we present the first results of ab initio DFT calculations for the structural and electronic properties of both thorite and huttonite by means of the full-potential linearized augmented-plane-wave method and the generalized gradient approximation (FLAPW-GGA). We will also focus on the ab initio DFT-based estimations of the comparative stability of thorite and huttonite as well as on stability of these polymorphs with respect to their constituent binary oxides (thorianite ThO_2 and SiO_2).

Moreover, we have calculated for the first time the theoretical shapes of X-ray emission (XES) (Si,O)-Kα,β spectra for thorite, huttonite as well as for SiO_2 and thorianite. It is well known, that XES is a powerful tool to probe the filled electronic states of materials depending from local chemical environment of excited atoms. Thus, while $ThSiO_4$ polymorphs often coexist in nature together with quartz and thorianite (Staatz and Brownfield 1982; Parnell and Eakin 1989) the theoretical analysis of their XES spectral shapes can be very useful not only for discussion of the applicability of this method to experimental establishing of the differences of electronic structures of these polymorphs, but also for conclusions about prospects of XES method for the characterization of various thorium-containing species and minerals.

Models and computational details

Thorite has a tetragonal structure isostructural to the zircon ($ZrSiO_4$, space group *I*41/*amd*) consisting of alternating {ThO_8} edge-sharing polyhedra and {SiO_4} tetrahedrons chains that are parallel to the *c*-axis (see Keller 1976). According to X-ray powder diffraction data (Taylor and Ewing 1978), thorite cell parameters are a = 7.129(1) Å and c = 6.319(1) Å.

The monazite-structured polymorph of thorium silicate, huttonite, adopt the monoclinic-symmetry structure (space group *P21/n*), and can be derived by introducing a ninth oxygen into the Th coordination sphere of the tetragonal (zircon-like) structure. For a detailed discussion of the geometrical parameters of monazite-like crystal structure (see, for example, Taylor and Ewing 1978; Mullica et al. 1985; Meldrum et al. 1999b). The lattice parameters of huttonite reported by Pabst et al. (1951) are a = 6.80 Å, b = 6.98 Å, c = 6.54 Å; β = 104.55 and are close to recently obtained data a = 6.774(2) Å, b = 6.962(2) Å, c = 6.495(3) Å; β = 105.0 (Mazeina et al. 2005).

The mentioned $ThSiO_4$ polymorphs: tetragonal thorite and monoclinic huttonite will be designated further as $ThSiO_4^{(t)}$ and $ThSiO_4^{(m)}$, respectively.

The constituent binary oxides: SiO_2 (α-quartz) and ThO_2 adopt the well-known hexagonal (space group $P3_221$) structure, consisting of an ordered trigonal lattice of interconnected {SiO_4} tetrahedrons (Wyckoff 1965; Will et al. 1988), and cubic fluorite-like (space group *Fm3m*) lattice with cubic site symmetry for the Th atoms and tetrahedral site symmetry for the oxygen atoms (Keller 1976), respectively.

The band-structure calculations of the all mentioned compounds were done by means of full-potential all-electron method with mixed basis APW + lo (FLAPW) as implemented in the WIEN2k program package (Blaha et al. 2001). The generalized gradient correction (GGA) to exchange-correlation potential of Perdew et al. (1996) was used. Concerning the relativistic effects, core states are treated fully relativistically in WIEN2k. For valence states a scalar relativistic scheme is used. The radii of not overlapped atomic spheres were 2.2 a.u. for Th, 1.4 a.u. for Si and 1.4 a.u. for oxygen. The plane-wave cutoff K_{cut} is determined by $R_{mt}K_{cut}$ = 9.0. The modified tetrahedron method (Blöchl et al. 1994) was employed for the density of states (DOS) calculations.

In result, for optimized geometries, the total, site- and *l*-projected DOSs, as well as energies of formation of Th silicates are obtained and analyzed. The theoretical shapes of XES (Si,O)Kβ,α spectra (Si—3p $\leftrightarrow$ s; O—2p $\leftrightarrow$ s transitions) were calculated using Fermi's golden rule and the matrix elements between the core and valence states (following the formalism of Schwarz and Neckel 1975); as implemented in the WIEN2k code. The calculated spectra include broadening for the spectrometer and core and valence lifetimes. These spectra provide information about the behavior of Si, O valence p-like states which participate in the Th–O and Si–O bonding and should elucidate the features of electronic states for $ThSiO_4$ polymorphs as compared with quartz and thorianite depending on a local atomic environment.

Results and discussion

Structural data

The calculated structural parameters for both $ThSiO_4$ polymorphs are summarized in Tables 1 and 2. The reported data corresponds to zero pressure and temperature $T = 0$ K. For $ThSiO_4^{(t)}$ and $ThSiO_4^{(m)}$ we optimized the atomic positions for the experimental lattice parameters a, b and c and relaxed all independent internal atomic coordinates until the respective forces were less than 0.5 mRy/a.u., and we find our results very similar to experiments (Taylor and Ewing 1978).

Our results for α-quartz (Tables 1, 2) are almost identical to those calculated by Zupan et al. (1998) which also used a full-potential LAPW method for the structural parameters of SiO_2, and compare well to the experimental data obtained by Will et al. (1988). Finally we also reproduce well the structural data for ThO_2 (see Keller 1976). Further these optimized structural data are used for our estimations of stability of $ThSiO_4$ polymorphs and for calculation of their electronic properties.

Table 1 Calculated lattice parameters (in nm) and atomic positions in the unit cells for thorite, huttonite and α-quartz in comparison with available experimental and theoretical data

Systems	Lattice parameters	Atomic positions
$ThSiO_4$ (thorite)	a = 0.7133[a]	Th (4a) 0 ¾ 1/8
	c = 0.6319[a]	Si (4b) 0 ¾ 5/8
		O (16h) 0 0.0723 0.2088
		0 0.0732[a] 0.2104[a]
$ThSiO_4$ (huttonite)	a = 0.6784[a]	Th (4e) 0.2797 0.1561 0.1024
	b = 0.6974[a]	0.2828[a] 0.1550[a] 0.0988[a]
	c = 0.6500[a]	Si (4e) 0.3029 0.1624 0.6146
		0.3020[a] 0.1616[a] 0.6117[a]
		O (4e) 0.3896 0.3400 05047
		0.3900[a] 0.3388[a] 0.4967[a]
		O (4e) 0.4825 0.1066 0.8268
		0.4803[a] 0.1060[a] 0.8234[a]
		O (4e) 0.1192 0.2132 0.7245
		0.1216[a] 0.2122[a] 0.7245[a]
		O (4e) 0.2475 0.4957 0.0693
		0.2451[a] 0.4976[a] 0.0626[a]
SiO_2 (α-quartz)	a = 0.5011	Si (3a) 0.4751 0 2/3
	0.4912[b]	0.4698[b] 0 2/3
	0.4990[c]	0.474[c] 0 2/3
	c = 0.5512	O (6c) 0.4174 0.2589 0.2077
	0.5404[b]	0.4151[b] 0.2675[b] 0.2139[b]
	0.5484[c]	0.413[c] 0.261[c] 0.210[c]

[a]Experimental, Taylor and Ewing (1978)

[b]Experimental, Will et al. (1988)

[c]Calculated from FLAPW method, Zupan et al. (1998)

Stability of $ThSiO_4$ polymorphs

One of the most interesting features of thorium silicate is that thorite with a high-symmetrical body-centered tetragonal unit cell ($ThSiO_4^{(t)}$) is a ground state phase (i.e., low-temperature α-polymorph), whereas the low-symmetrical monoclinic $ThSiO_4^{(m)}$ is the high-temperature β-polymorph (huttonite). Thus, the phase transition (at around 1,480 K, see Finch et al. 1964; Keller 1976; Seydoux and Montel 1997) from tetragonal $ThSiO_4^{(t)}$ to monoclinic $ThSiO_4^{(m)}$ occurs, in contrary to the general law that the less dense modification exists at higher temperatures.

On the other hand, both thorite and huttonite which occur naturally in igneous and metamorphic rocks, as inclusions or accessory minerals (see Broska et al. 2000; Förster et al. 2000; Mordberg 2004; Johan and Johan 2005 and references therein) appear to be thermodynamically metastable relative to their constituent binary oxides: SiO_2 (quartz) and ThO_2 (thorianite) at ambient conditions (Mazeina et al. 2005). Thorium silicate polymorphs presumably can be stabilizing at high temperature by the entropy factor (Mazeina et al. 2005) or by some impurities which replace thorium or silicon (Keller 1976; Lumpkin and Chakoumakos 1988; Hansley and Fitzpatrick 1989). Recently, the introduction of about 10 mol% cerium to stabilize the synthetic $ThSiO_4^{(t)}$ phase was successfully used (Grover and Tyagi 2005; Grover et al. 2005).

In order to estimate the relative stability of $ThSiO_4^{(t,m)}$ phases, their Gibbs free energies ($G = E^0 + PV - TS$) should be obtained. Since all our calculations are performed at zero temperature and zero pressure conditions, the G becomes equal to the E^0 and the value of $\Delta E_{tot} = \{E_{tot}(ThSiO_4^{(t)}) - E_{tot}(ThSiO_4^{(m)})\}$ may be used for comparative estimation of stability of these polymorphs.

In this way, we have obtained $\Delta E_{tot} = -0.0533$ eV/form.unit (i.e., –5.1434 kJ/mol); thus for thorium silicate the tetragonal phase (thorite) became more favorable than monoclinic structure, arising in huttonite. It is interesting that our estimation of the relative stability of $ThSiO_4^{(t,m)}$ phases (at about 5.1 kJ/mol) is comparable with experimentally measured (by high-temperature oxide-melt calorimetry) enthalpy of the thorite–huttonite phase transition ($\Delta H_{pt} \sim 6.7 \pm 2.5$ kJ/mol) obtained recently by Mazeina et al. (2005), however is much less than the earlier data: $\Delta H_{pt} \sim 23.4$ kJ/mol (Dachille and Roy 1964) and $\Delta H_{pt} \sim 18$ kJ/mol (Seydoux and Montel 1997). Naturally the thermodynamic factors such as temperature and pressure should be taken into account by such comparisons.

Table 2 The bond lengths (nm) and bond angles (deg) for thorite, huttonite, α-quartz and thorianite according our FLAPW-GGA calculations

Parameters		$ThSiO_4$ (thorite)	$ThSiO_4$ (huttonite)	SiO_2 (α-quartz)	ThO_2 (thorianite)
Bond lengths	R(Th–Si)	0.3159	0.3215	–	–
	R(Si–O)	0.1646	0.1635 (0.1639[a])	0.1631 (0.1628[a])	–
	R(Th–O)	0.2359	0.2383 (0.2414[a])	–	0.2435
Bond angles	O–Si–O	100.73	99.81	146.01	–
	O–Th–O	92.89	73.24	–	90

[a]For huttonite and α-quartz two types of non-equivalent Th–O and Si–O bonds: in $\{ThO_8 + O\}$ polyhedron and in distorted SiO_4 tetrahedrons are presented

Next, we have studied the comparative stability of each polymorph: $ThSiO_4^{(t)}$ or $ThSiO_4^{(m)}$ with respect to reference oxides ThO_2 and SiO_2, in formal reactions $ThSiO_4^{(t,m)} \leftrightarrow ThO_2 + SiO_2$. For this purpose their energies of formation ΔH^0 (in conditions: $P = T = 0$) have been calculated as:

$$\Delta H^0 = E_{\text{tot}}\left(\text{ThSiO}_4^{(\text{t,m})}\right) - \{E_{\text{tot}}(\text{ThO}_2) + E_{\text{tot}}(\text{SiO}_2)\} \quad (1)$$

In Eq. 1, E_{tot} are the total energies at the optimized geometries of the $ThSiO_4^{(t,m)}$, ThO_2 and α-quartz, obtained in our FLAPW-GGA calculations. According to our calculations, the ΔH^0 values are small but positive: + 0.026 eV/form.unit (~ 2.5 kJ/mol) and + 0.079 eV/form.unit (~ 7.6 kJ/mol) for $ThSiO_4^{(t)}$ and $ThSiO_4^{(m)}$, respectively. Thus, our results clearly show that at zero temperature and zero pressure approximation both thorite and huttonite have the positive energies of formation, i.e., these phases are unstable in comparison with mechanical mixture of constituent binary oxides. These results provide additional evidences that both $ThSiO_4^{(t,m)}$ polymorphs often coexist in nature together with quartz and thorianite (see, for example, Staatz and Brownfield 1982; Parnell and Eakin 1989). Note, that the enthalpies of formation ΔH (at 298 K) of thorite and huttonite, synthesized using flux-method from binary oxides, as derived from the calorimetric data (Mazeina et al. 2005) are 19.6±2.0 and 26.3±3.0 kJ/mol.

Electronic properties

The total, site- and *l*-projected DOS of both $ThSiO_4^{(t,m)}$ polymorphs together with the DOS for constituent binary oxides: SiO_2 and ThO_2 as obtained from our FLAPW-GGA calculations are given in Fig. 1.

For α-quartz our data reproduce the well-known picture (see, for example, Xu and Ching 1991), where the bottom of conduction band is formed mainly by

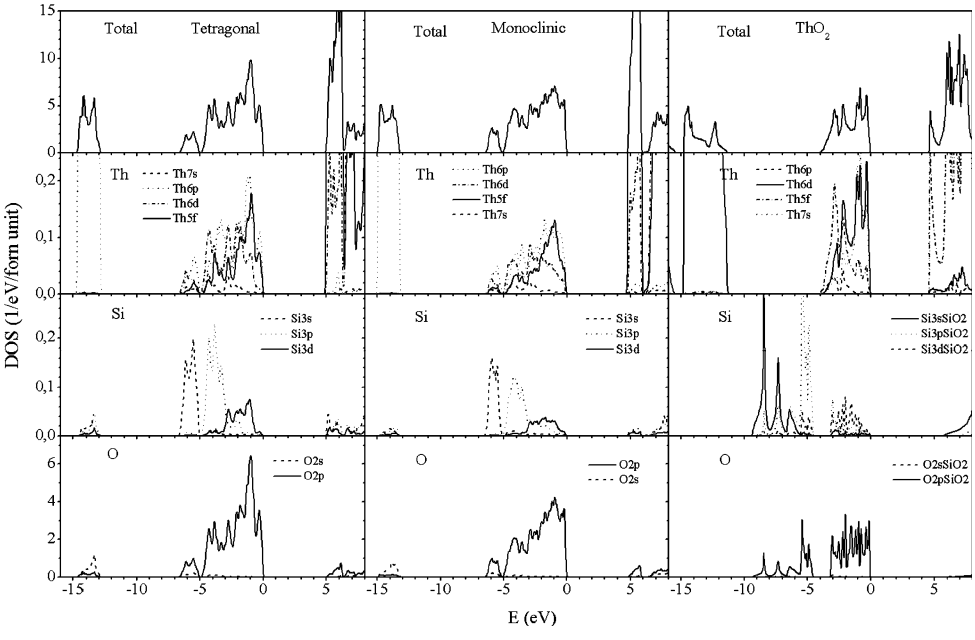

Fig. 1 Densities of states for thorite (*1*), huttonite (*2*) in comparison with thorianite (*3*) and α-quartz (*4*). For thorite and huttonite the total (*upper panels*) and (Th, Si, O) *l*-projected DOS are depicted. For ThO_2 the total and Th *l*-projected DOS; and for α-quartz—Si and oxygen *l*-projected DOS are presented

Si3s states, while the valence band (VB)—by O2p states. As presented in Fig. 2, the admixtures of Si3s,3p,3d orbitals in VB exists, and the Si–O bonding in α-quartz determined by hybridization of these states. In turn, the VB is divided into two parts (A and B) by gap about 1.7 eV, where the upper band (A) consists mainly from the non-bonding O2p states whereas the lower band (B) from bonding O2p states. The O2s states (are not shown in Fig. 1) are located much lower, in the interval between –17 and –20 eV below the Fermi level (E_F).

In Fig. 1, the DOS for thorianite is also presented, where three separate groups of electronic bands are clearly visible. Two of them are located between –18.8 and –16.1 eV and between –14.7 and –11.2 eV below E_F, and are predominantly of O2s and Th6p types, respectively. The upper VB in the energy range from –4.1 eV up to E_F has mainly O2p character. These results are in reasonable agreement with other works devoted to ThO_2 electronic structure (Ellis et al. 1989; Terki et al. 2005b).

Note, that there are appreciable contributions from Th6d states in this energy range due to Th–O hybridization indicating the presence of a covalent bonding. Additionally, the Th5f states bring some contribution into occupied near-Fermi region (Fig. 1). The bottom of conduction band, which is separated from the VB by a gap (at about 4.8 eV) consists essentially of Th6d,5f states with admixtures of O2p antibonding orbitals.

Let us discuss the electronic properties of Th silicate polymorphs. For $ThSiO_4^{(t)}$, one can clearly distinguish three separate VBs. Two of them are located between – 18.5 and – 16.6 eV and between – 14.8 and – 12.9 eV and are of O2s and Th6p types, respectively. The highest VB is placed from – 6.8 eV up to Fermi level and is composed mainly of O2p orbitals. The band gap (BG) for $ThSiO_4^{(t)}$ is found at about 4.9 eV. As compared with constituent binary oxides the BG for thorite is closer to thorianite (BG ~ 4.75 eV) than to SiO_2 (BG ~ 5.61 eV). The bottom of the conduction band consists of the Th5f orbitals, followed by the bands with Th6d character.

According to the data obtained, the interatomic bonds for $ThSiO_4^{(t)}$ are due to the mixing of oxygen 2p orbitals with Si3s,3p,3d and thorium 6d and 5f orbitals. Note that as for metallic thorium (Veal et al. 1973; Koelling and Freeman 1975; Gasche et al. 1996) as well as for thorianite, the Th5f states in thorite are itinerant and they partially overlap with occupied O2p bands. Thus, a considerable covalency occurs between Th–O and Si–O atoms, and thorite is far from the idealized ionic picture, which supposed the purely ionic bonding between the cations Th^{4+} and $(SiO_4)^{4-}$ units without any orbital hybridization. We notice also the presence of Th6p and O2s contributions into O2s and Th6p bands, respectively. This agrees with assumption (Teterin et al. 2000) that these orbitals may participate in chemical bonding.

In general, the similar pictures for electronic spectrum and orbital hybridization effects were obtained also for huttonite (Fig. 1). The main differences, arising in band structure of $ThSiO_4$ polymorphs when going from thorite to huttonite is the narrowing of BG (at about 0.2 eV) and some smoothing of total DOS profile for monoclinic huttonite which occurs as a result of lowering of overall crystal symmetry when a ninth oxygen incorporate into the coordination sphere of thorium, leading to and a distortion of the $\{SiO_4\}$ tetrahedra. Thus, the DOS for huttonite may be considered as "intermediate" in the crystalline-to-amorphous transition of thorite, which can be achieved, for example, under heavy-ion irradiation (Meldrum et al. 1999b).

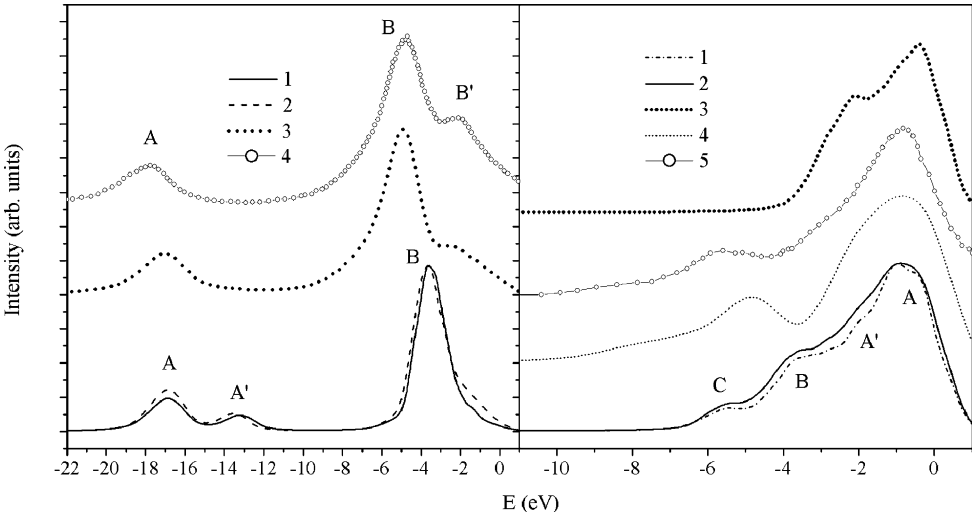

Fig. 2 *Left*—calculated Si Kβ XES spectra for thorite (*1*), huttonite (*2*) and α-quartz (*3*); the experimental spectrum for quartz (*4*; adapted from Wiech and Kurmaev 1985) is also depicted. *Right*—calculated O Kα XES spectra for thorite (*1*), huttonite (*2*), thorianite (*3*) and α-quartz (*4*); the experimental O Kα spectrum for quartz (*5*; adapted from Klein and Chun 1972) is also shown

Finally, the BG values are among the most important parameters for a number of applications of the $ASiO_4$ silicates, which belong to the wide-band-gap oxides.

Meanwhile it is well known that first principles band-structure methods using the local density approximation (LDA) and the related generalized approximation (GGA) give a very reasonable results for the ground state properties (such as structural parameters, total energies, etc.), but lead to a typical underestimating of the BG for semiconducting or insulating materials—at about 30–50% (Sham and Schluter 1983; Terki et al. 2005a; Robertson et al. 2006).

Our FLAPW-GGA data for α-quartz gives a value of BG = 5.61 eV (indirect K–Γ transition) in excellent agreement with results of others LDA calculations (e.g., BG = 5.59 eV, Xu and Ching 1991; BG = 5.84 eV, Gnani et al. 2000; BG = 5.38 eV, Samantaray et al. 2004) but differs considerably from the experimental gap which is about 8.9 eV, see, for example, Klein and Chun (1972) or the references in Xu and Ching (1991).

A standard empirical correction means a fitting of the LDA gap to a experimental value (Tang et al. 1998). For SiO_2 and some silicates such a correction factor was estimated at 1.6 (Samantaray et al. 2004). In our case, a very close multiplicative correction factor (1.59) brings the LDA BG for α-quartz to experimentally measured gap. Thus, taking into account this factor, it is possible to estimate the ''experimental'' values of thorite and huttonite gaps, which will at about 7.8 and 7.6 eV, respectively. Note that BGs for zircon and hafnon are lower: 6.5–7.1 eV and at about 6.0 eV, respectively (see Robertson et al. 2006).

X-ray emission spectra

As is known, the intensity (I) of the XES spectra in the dipole approximation is determined by the DOS and the matrix elements and can be written as

$$I(E,\mathbf{e}) \approx E^3 \times \sum |\langle \mathrm{f}|\mathbf{e}\cdot\mathbf{r}|\mathrm{i}\rangle|^2 \times \delta(\mathrm{E}_f + \mathrm{E} - \mathrm{E}_i) \qquad (2)$$

where ⟨f| and |i⟩ refer to the final and initial one-electron states, E_i and E_f are the corresponding energy eigenvalues of the states involved in the transition. In our case, oxygen Kα (2p → 1s transition) and silicon Kβ (3p → 1s transition) XES probe directly the distributions of occupied B2p and Si3p DOSs.

Figure 2 shows the experimental XES Si Kβ-edge spectrum in α-quartz (Wiech and Kurmaev 1985) in comparison with our theoretical spectra for SiO_2, thorite and huttonite as obtained from FLAPW-GGA calculation. The spectra are depicted by aligning to the Fermi level. It can be seen that the experimental Si Kβ XES for SiO_2 is reasonable reproduced by the band-structure calculations, enabling to attribute each spectral peak to individual electronic bands. Namely, the two main peaks A and B separated by gap ~ 13.1 eV arise from the admixture of Si states into O2s and bonding O2p bands, and an additional sub-peak B′ which is located above the most intense peak B, arise from Si3p contribution to non-bonding O2p band. Going from α-quartz to Th silicates the Si K spectral shapes change considerably. The main peak B has narrowed and shifted to lower binding energies by 1.1 eV, without any pronounced substructure. On the contrary, in the region at about 13 eV below the Fermi level, an additional peak A′ appear. This peak originates from the Si states contribution to Th6p band.

The O Kα spectral shapes (reflect the occupied O2p states) of $ThSiO_4$ polymorphs are found also to be quite different in comparison with binary oxides: SiO_2 and ThO_2 (\Fig. 2). In contrary to two-peak spectra of these oxides, for Th silicate at least three maxima (A, B and C, for huttonite) became visible. For thorite, the additional sub-peak A′ is placed at about 2.2 eV below E_F. At the same time, except the mentioned feature, the Si Kβ- as well as the O Kα spectral shapes for both $ThSiO_4$ polymorphs appear rather similar.

Thus, our data shows that both O Kα and Si K XES of thorite and huttonite differ drastically compared to quartz and thorianite, i.e., the XES spectroscopy near the Si Kβ, O Kα edge may be very useful technique not only for detailed investigation of the bulk-electronic structure of Th silicates but also for the phase analysis of complex mineral samples containing these species.

Conclusions

We use the first-principle FLAPW-GGA approach to investigate the structural, electronic properties, stability and XES spectra of thorium silicate polymorphs (thorite and huttonite) in comparison with their constituent binary oxides: thorianite ThO_2 and α-quartz SiO_2. It was shown that both polymorphs are wide-band-gap semiconductors: the corrected LDA gaps for thorite and huttonite are estimated at about 7.8 and 7.6 eV, respectively. Our calculations predict that the thorium 5f states contribute into occupied near-Fermi region, i.e., these orbitals in $ThSiO_4$ are participate in Th–O bonding due to partial overlapping with occupied O2p states.

We find that thorite with a high-symmetrical body-centered tetragonal cell became more favorable than huttonite with monoclinic structure (at about 5.1 kJ/mol). On the other hand, our first-principle calculations show that at zero temperature and zero pressure approximation both thorite and huttonite have the positive energies of formation (at about 2.5 and 7.6 kJ/mol, respectively)—with respect to ThO_2 and SiO_2; i.e., these phases are unstable in comparison with mechanical mixture of constituent binary oxides.

Finally, the theoretically predicted shapes of the O Kα, Si Kβ XES spectra for thorite and huttonite demonstrate a set of differences from the corresponding emission lines for thorianite and quartz, reflecting the specific features of local Th–O and Si–O bonds in these polymorphs. Based on these results, it may be assumed that XES technique will be useful as for the study of electronic properties as well as for phase analysis of complex silicates.

Acknowledgments This work was supported by the Russian Foundation for Basic Research, Grant No. 06-08-00808.

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