Analysis of UV-Visible Absorption Spectra for Quartz and Topaz in Silicate Minerals by MO Calculations Using the Cluster Model Molecules

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This study aims to clarify the electronic state of the UV-visible absorption spectra of smoky quartz, yellow topaz and pink topaz as the trapped hole defect centers due to aluminum or chromium substitution in silicate minerals. We calculated the tetrahedral cluster models ($AlH_{12}O_{16}Si_4$) for smoky α-quartz, and the octahedral types ($Al_3F_4H_4O_8$, $AlCrF_4H_4O_8Si$) for (yellow and pink topaz), respectively, using the *ab initio* GAUSSIAN program. The calculations for the colored models were performed using the unrestricted Hartree-Fock MO method with 6-311G (2d, 2p) basis in the program. The theoretical transition energies at around 380, 500, and (430, 470, 590) nm for the model molecules of smoky quartz, yellow topaz and pink topaz, respectively with single excitation configuration interaction (CIS) method enable us to correspond to the experimental absorption spectra. We will analyze the absorption peaks for the quartz and topaz from the transition energies between MOs, and discuss the electronic state from coefficients of the atomic orbitals (AO)s.

INTRODUCTION

Lattice defects in silica crystal have been extensively studied for over four decades, mainly for their technological importance. However, in the past fifteen years one has developed in detail from theoretical and experimental atomic models for these defects [1-6]. It is well-known that we can use optical absorption and electron spin resonance (ESR) for investigating such defects in insulators. Here, we aim to clarify the information about the electronic state of colored crystals (natural smoky quartz, yellow and pink topaz) from analysis of the optical absorption by *ab initio* MO calculations using the cluster models.

Quartz is a tectosilicate, having all corners of the tetrahedral shared, and it is a hexagonal structure which may accommodate interstitial cations. The model for the defect center in irradiated quartz is known to be due to an Al impurity having replaced by a four-coordinated Si atom. The defect center for the existence of a fully localized hole (a hole trapped

in a nonbonding 2p orbital of an O atom adjacent to Al) at sufficiently low temperatures was shown from accurate ESR analysis. In the work, Nuttall and coworker determined particularly the hyperfine coupling constants with the ^{27}Al, ^{29}Si and ^{17}O nuclei [7]. Above room temperature, the hole jumps rapidly among all four adjacent O atoms. For the observed absorption of natural smoky quartz, the spectrum ranges from UV to infrared, although the peak is at around 470 nm. On the other hand, topaz is a naturally occurring silicate gemstone usually found in large clear crystals, but occasionally colored by transition-metal impurities. The formula unit is ($[Al(OH, F)]_2SiO_4$) as an aluminum fluorosilicate, and the orthorhombic unit cell, with dimensions $a = 4.64$ Å, $b = 8.80$ Å, and $c = 8.38$ Å, contains four formula units. There have been several studies [8, 9] which dealt with the defect in topaz due to the fast-neutron irradiation. As far as we know, there is no work for analyzing the absorption spectra of natural

smoky quartz and yellow and pink topaz using MO theory.

In the present study, we examine the electronic state of the UV-visible absorption spectra using tetrahedral cluster models ($H_{12}O_{16}Si_5$, $AlH_{12}O_{16}Si_4$) for (transparent, smoky α-quartz), and the octahedral types (Al_2FH_7-$O_{11}Si$, $Al_3FH_7O_{11}$, $AlCrFH_7O_{11}Si$) for (transparent, yellow and pink topaz), respectively, by the *ab initio* method. In the model clusters of smoky quartz, yellow and pink topaz, the absorption spectra are calculated by the unrestricted Hartree-Fock (UHF) single excitation configuration interaction (CIS) method in GAUSSIAN 98 program.

EXPERIMENTAL

We used yellow and pink topaz crystals available from Ouro Preto. In order to obtain the UV and visible absorption spectra of the topaz, we used a Cary Model 14PM Recording Spectrophotometer. We cited the experimental UV visible absorption spectrum of smoky quartz referred to D.P. Partlow and Cohen [10].

CALCULATION METHOD

We used the restricted (R) and unrestricted (U) Hartree-Fock calculations with the single excitation configuration interaction (CIS) method to analyze the experimental absorption spectra for quartz and topaz in silica minerals. In the CIS method, the total wave function is written as a linear combination of all possible singly excited determinants. Then, we need to consider the size of cluster models in the RHF and UHF MO calculations with the CIS method from the limit of computer size and the calculation times in our workstation. In order to obtain the reasonable model cluster for transparent quartz, we calculated the RHF MO calculations of model clusters, $Si_{17}O_{52}H_{36}$ and $Si_5O_{16}H_{12}$ at the ground state, and got that densities (p_{xx}, p_{yy} and p_{zz}) of 3p electrons in inner five Si atoms of $Si_{17}O_{52}H_{36}$ are similar values to those in five Si atoms of $Si_5O_{16}H_{12}$. In the Hartree-Fock calculations, we, thus, assumed this kind of "chemical distinction" for the model $Si_5O_{16}H_{12}$ cluster does not reflect in a different electronic structure of the defect.

The calculations have been performed within the cluster model approach. The cluster dangling bonds

have been saturated with H atoms. The positions of the cluster atoms were fixed to those of quartz, and topaz referred to X-ray diffraction data [11, 12]. We cited that in pure quartz, each Si cation is surrounded by O anions, with the bond distance: Si-O = 1.6123 Å, and there is tetrahedral symmetry at the cation. In the positions of Al, or Cr atom for model clusters of smoky quartz, yellow and pink topaz, we substituted the central site Si with Al for cluster $H_{12}O_{16}Si_5$, a site Si atom in question with Al for cluster $Al_2FH_7O_{11}Si$, and a site Al atom in question with Cr for cluster $Al_2FH_7O_{11}Si$, respectively. The model clusters are $H_{12}O_{16}Si_5$, and $AlH_{12}O_{16}Si_4$ for transparent, smoky α-quartz, and $Al_2FH_7O_{11}Si$, $Al_3FH_7O_{11}$, and $AlCrFH_7O_{11}Si$ for transparent, yellow, and pink topaz, respectively. These clusters are terminated by O-H for quartz, and by O-H, or partially F groups, for topaz, respectively.

For the calculations of UV-V absorption spectra, the electronic states of smoky quartz, yellow topaz and pink topaz were obtained using the CIS calculations of the model cluster molecules in GAUSSIAN98 program with 6-311G (2d, 2p) bases for all atoms. The UV-visible absorption spectra were simulated by the superposition of a peak centered on the shifted energy values, E_k. The peak shape is represented by a Gaussian lineshape function:

$$F(x) = A(k)\exp\left\{-B(k)(x - E_k)^2\right\} \qquad (1)$$

where the intensity, $A(k)$, is estimated from the transition probabilities. For $B(k)$, we used a constant linewidth of 0.35 eV. For a best fit of simulated spectra with observed ones, we shifted the energy levels with 0.80 eV for quartz and 0.90 eV for topaz, respectively.

RESULTS AND DISCUSSION

UV-visible absorption spectra of smoky quartz

In order to determine the electronic state of UV and visible absorption spectra for transparent and smoky quartz, we performed *ab initio* MO calculations using model clusters $H_{12}O_{16}Si_5$, and $AlH_{12}O_{16}Si_4$, respectively. The calculated absorption peaks were estimated as 200 and 380 nm for transparent and smoky quartz, respectively in Fig. 1 (a). Fig. 1 (a) also includes the experimental absorption peak of smoky
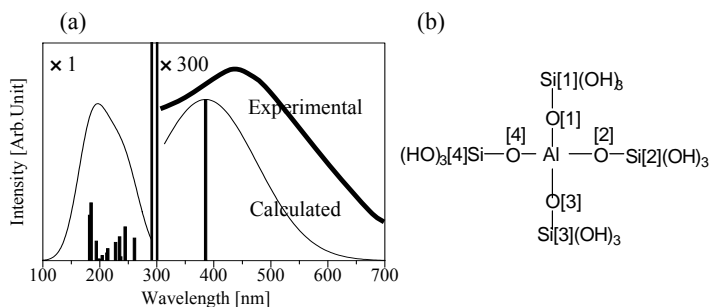
Fig.1. (a) Theoretical UV-V absorption spectrum of smoky quartz with experimental one, (b) Model molecule of smoky quartz

Table 1. spin densities of each atoms in

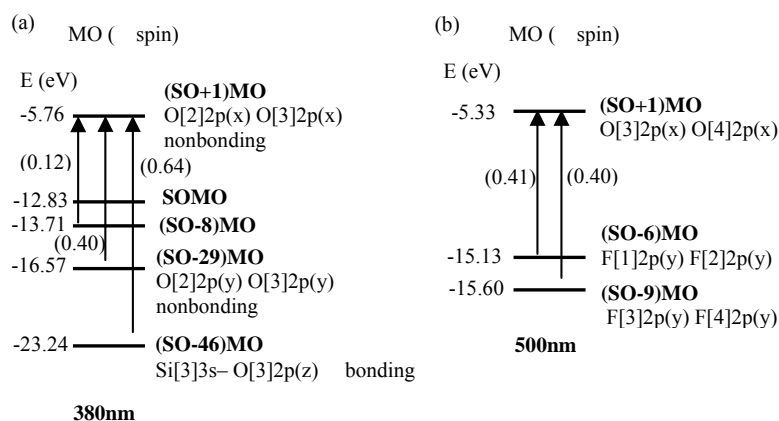| Atom [number]	Total spin densities	Main contribution of AO spin density
Al	0.0	
O [1,2,4]	0.0	
O[3]	1.0	$0.5 (p_y, p_z)$
Si[1,2]	0.0	
Si[3,4]	0.0	
eigenvalue of S^2	0.75	0.75

Fig.2 MO diagram and main CI expansion coefficients of (a) smoky quartz and (b) yellow topaz

quartz, and Fig. 1 (b) shows the chemical formula of the model. The theoretical spectrum of the model for smoky quartz is able to correspond to the experimental one. We can, then, see from our calculations using model clusters that the origin for the peak of smoky quartz is due to substituting the central site Si with Al for cluster $H_{12}O_{16}Si_5$. Then, let us consider the nature of the absorption from MO theory. Table1 shows spin densities of each atom from the model cluster $AlH_{12}O_{16}Si_4$ of smoky quartz by unrestricted CIS method. In the model, the unpaired electron is on nonbonding p orbital of O atom (No. 3 Fig. 1 (b)) bonded to Al. We obtained that the experimental transition which corresponds to 450 nm is mainly from lower 46th $p\sigma$(O 2p-Si 3s) bonding MO (from SOMO), or 29th $p\sigma$(Si 3p-O 2p) bonding MO (from SOMO) to (lone-pair nonbonding of O 2p)* LUMO in No.2 or 3 oxygen atom, as shown in Fig. 2 (a).

UV-visible absorption spectra of yellow topaz

We estimated the absorption peaks as 290 and 500 nm from *ab initio* MO calculations using model cluster $Al_2F_4H_4O_8Si$, and $Al_3F_4H_4O_8$ for transparent and yellow topaz, respectively. In the case of yellow topaz, we showed the experimental and theoretical spectra, and the chemical formula of the model in Fig. 3 (a) and (b), respectively. The theoretical spectrum enables us to correspond to the experimental one. We show spin densities of each atom for $Al_3F_4H_4O_8$ in Table 2 from calculations of the model cluster by unrestricted CIS method. Although the eigenvalue of S^2 is unsatisfied as 3.75, we can see unpaired electrons may be on no-bonding p orbitals of O atoms bonded to No.2 and 3 Al atoms in Fig.3 (b). For the absorption energy of 500 nm, we obtained two components of transitions calculated by the UHF calculations. In Fig. 2 (b), the one is lower 9th $p\pi$-like(F 2p-Al 3p) bonding MOs (from SOMO) in No 3 and 4 F atoms bonded to No. 2 and 3 Al atoms to the
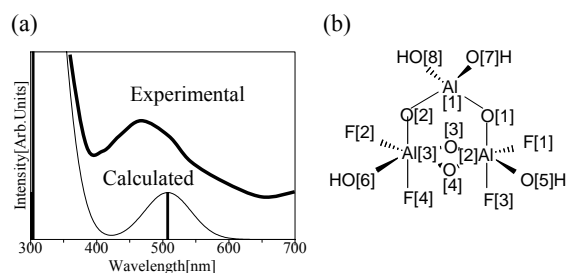
Fig.3. (a) Theoretical UV-V absorption spectrum of yellow topaz with experimental one, (b) Model
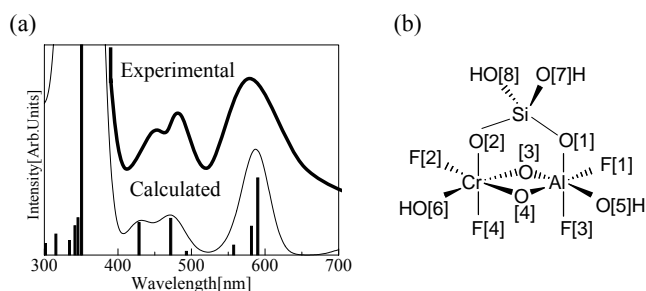

Fig.4. (a) Theoretical UV-V absorption spectrum of pink topaz with experimental one, (b) Model molecule of pink topaz (b)

Table 2. Spin densities of each atoms in yellow topaz.

Atom [number]	Total spin densities	Main contribution of AO spin density
Al[1,2,3]	0.0	
O [1,2]	1.0	0.5 (py)
O [3]	1.0	0.4 (pz)
O [4]	2.0	1.0 (px,pz)
O [5,6]	1.1	0.5 (px,pz)
O [7,8]	0.0	
F[1,2,3,4]	0.0	
eigen value of S^2	5.78 3.75	

Table 3. Spin densities of each atoms in pink topaz.

Atom [number]	Total spin densities	Main contribution of AO spin density
Si	0.0	
Al	0.10	
Cr	0.4	
O[1,2]	1.1	0.5 (py)
O[3,4]	1.0	0.4 (pz)
O[7,8]	0.0	
F[1,2,3,4]	0.0	
eigenvalue of S^2	9.06 8.75	

(lone-pair nonbonding O2p)* LUMO in No.3 and 4 O atoms bridged between No.2 and 3 Al atoms, and the other is from lower 6th pπ-like (F 2p-Al 3p) bonding MOs (from SOMO) in No. 1 and 2 F atoms bonded to No. 2 and 3 Al atoms to (lone-pair nonbonding O2p)* LUMO in No.3 and 4 O atoms bridged between No.2 and 3 Al atoms.

UV-visible absorption spectra of pink topaz

For pink topaz, the absorption peaks were estimated as 430, 470 and 590nm using $AlCrFH_7O_{11}Si$ model molecule with unrestricted CIS method to simulate UV and visible spectra. Fig. 4 (a) shows that the theoretical spectrum of the model is in a considerably good agreement with experimental one. We can see from our calculation using the model cluster that the origin for the peak of pink topaz is due to substituting a site Al atom with Cr for cluster $Al_2F_4H_4O_8Si$. Table 3 shows spin densities on nonbonding p orbitals of O atoms in pink topaz. The unpaired electron is on NO. 1, 2, {3, 4} oxygen

atoms bridged among (Si, Al), (Si, Cr), and {Al, Cr} atoms, respectively in the cluster model in Fig. 4 (b). Then, we indicated the nature of the absorption from MO theory in Fig. 5. In the figure, the peak at around 430 nm is due to the absorption energy from lower 27th pσ (O2p-Al3s) bonding MO (from SOMO) in No.5 O atom, and from lower 9th lone-pair nonbonding F 2p orbitals in No. (1, 3), or No. (2, 4) F atoms bonded Al, or Cr atom, respectively to higher 3rd pπ*(O 2p-Al 3p), or dpπ*(O 2p-Cr 3d) bonding MO (from LUMO) in NO. (1, 3), or (2, 4) O atoms bonded to Al , or Cr atom, respectively. The peak at around 470nm results from lower 33th dpπ(Cr 3d-O 2p, F 2p) and 10th dpπ(Cr 3d-O 2p) bonding MOs (from SOMO) to higher 2nd (lone-pair nonbonding Cr 3d)* MO (from LUMO). The 3rd peak at around 590nm is owing to the absorption energy from lower 1st (lone-pair nonbonding O 2p) MO (from SOMO) to anti pπ(Cr 3d-O 2p)* LUMO, and from dpπ (Cr 3d-O 2p) SOMO to 2nd (nonbonding Cr 3d)* MO (from LUMO).

MO(spin)

MO(spin)

E (eV)

E (eV)

E (eV)

(a) 430nm column:

-0.88 — **(SO+3)MO**
O[1]:2p(z)-O[3]:2p(z)
-O[4]:2p(z)-O[5]:2p(z)
dpπ, or pπ bonding*

-10.22 — **SOMO**
Cr:d(z^2)-O[6]2p(z)
bonding

-15.99 — **(SO-9)MO**
F[1]:2p(x),F[2]:2p(x),
F[3]:2p(x),F[4]:2p(x)
nonbonding

-19.98 — **(SO-27)MO**
Al:3s-O[5]:2p(y)
bonding

430nm

(b) 470nm column:

1.40 — **(SO+3)MO**
Cr:d(x^2-y^2)
Nonbonding*

-10.24 — **SOMO**

-16.48 — **(SO-10)MO**
Cr:d(zx) O[6]2p(z)
dpπ bonding

-22.23 — **(SO-33)MO**
Cr:d(zx)-O[2]:2p(z)-
F[2]:2p(z) dpπ bonding

470nm

(c) 590nm column:

1.40 — **(SO+3)MO**
Cr:d(x^2-y^2)

3.01 — **(SO+1)MO**
Cr:d(xy)-O[6]2p(x)
Anti d pπ bonding

(0.32)

(0.35)

10.24 — **SOMO**
Cr:d(xy)-O[6]2p(x)
dpπ bonding

14.37 — **(SO-1)MO**
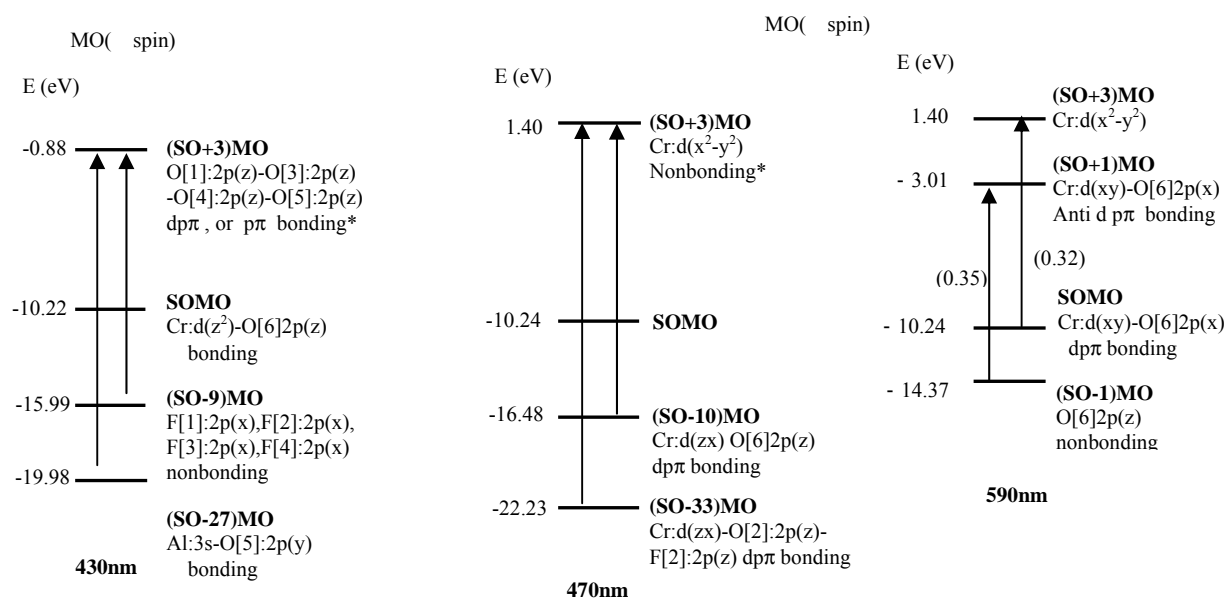O[6]2p(z)
nonbonding

590nm

Fig.5. MO diagram and main CI expansion coefficients of pink topaz. (a) around 430nm ,(b) around 470nm (c) around 590nm

CONCLUSIONS

We performed *ab initio* MO calculations using $AlH_{12}O_{16}Si_4$, $Al_3F_4H_4O_8$, and $AlCrF_4H_4O_8Si$ model clusters for smoky quartz, yellow and pink topaz, respectively, with unrestricted CIS method to simulate UV and visible spectra. From our calculation the origin for the peak of smoky quartz, yellow and pink topaz is due to substituting the central site Si with Al for cluster $H_{12}O_{16}Si_5$, a site Si atom with Al for cluster $Al_2F_4H_4O_8Si$, and a site Al atom with Cr for cluster $Al_2F_4H_4O_8Si$, respectively. We analyzed the absorption peaks for the quartz and topaz from the transition energies between MOs, and discussed the electronic state from coefficients of AOs.

A hole trapped in a nonbonding 2p orbital of an O atom adjacent to Al in quartz shown from accurate ESR analysis is illustrated by our UHF calculations with CIS using model molecules.

REFERENCES

[1] D. L. Griscom, in Defects in Glasses, edited by F. L. Galeener, D. L. Griscom (Materials Research Society, Pittsburgh, PA, 1986), Vol. 61, pp. 213-221.

[2] A. H. Edwards, in Defects in Glasses, edited by F. L. Galeener, D. L. Griscom (Materials Research Society, Pittsburgh, PA, 1986), Vol. 61, pp. 3-20.

[3] J. Robertson, Phil. Mag., **B 52**, 371 (1985).

[4] P. S. Rao, R. J. McEachern, and J. A. Weil, J. Comput. Chem., **12**, 254 (1991).

[5] F. Sim, C. R. A. Catlow, M. Dupuis, and J. D. Watts, J. Chem. Phys., **95**, 4215 (1991).

[6] M. Martini, A. Paleari, G. Spinolo, and A. Vedda, Phys. Rev., **B52**, 138 (1995).

[7] R. H. D. Nuttall and J. A. Weil, Can. J. Phys., **59**, 1696 (1981).

[8] V. Priest, D. L. Cowan, D. G. Reichel and F. K. Ross, J. Appl. Phys., **68**, 3035 (1990).

[9] V. Priest, D. L. Cowan, H. Yasar, and F. K. Ross, Phys. Rev., **B44**, 9877 (1991).

[10] D. P. Partlow, and A. J. Cohen, Amer. Mineral., **71**, 589 (1986).

[11] G. S. Smith, and L. E. Alexander, Acta. Cryst., **16**, 462 (1963).

[12] P. H. Ribbe, and G. V. Gibbs, Amer. Mineral., **56**, 24 (1971).