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Molecular orbital approach to the optical nonlinearities of fresnoite-type crystals

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Abstract

Hyperpolarizability (β) values have been evaluated by means of molecular orbital calculation for the clusters which simulate the fresnoit type crystals, $Ba_2TiGe_2O_8$(BTG), $Ba_2TiSi_2O_8$ (BTS), and $Sr_2TiSi_2O_8$ (STS). The experimental results have suggested that the second order optical nonlinearity of the crystals were strongly affected by the distortion of the crystal structure. In this study, β values were calculated for distorted clusters of BTG, BTS, and STS crystals. The obtained β values increase both with axial (*c*-axis direction) and equatorial (in *c*-plane) expansions of the unit cell. Especially, the β value of BTG cluster increased significantly with axial expansion.

Keywords: Optical nonlinearity; Glass ceramics

1. Introduction

Development of new inorganic nonlinear optical materials is desired for the future photonics. They are expected to have high performance in wavelength conversion, electro-optic effect, and so on, and to keep the their nonlinearity steadily and parmanently.

Fujiwara et al.[1,2] suggested that transparent suface-crustallized glasses and glass-ceramics containing nonlinear optical/ferroelectric crystals can be candidates of such materials. Takahashi et al.[3–5] have developed transparent surface-crystallized glasses containing of fresnoit-type crystals; $Ba_2TiGe_2O_8$ (BTG), $Ba_2TiSi_2O_8$ (BTS), and $Sr_2TiSi_2O_8$ (STS) and have demonstrated that these materials exhibit quite high optical nonlinearity. The strength of the nonlinearity is in the order of BTG > BTS > STS, and it is parallel to the order of *c*/*a* ratio of their unit cell.

The origin of the optical nonlinearity of these crystals is TiO_5 unit in the fresnoit-type structure. The above relationship between optical nonlinearity and *c*/*a* ratio suggests that the strength of optical nonlinearity depends on the dimension of the unit cell rather than the choice of elements (Ba or Sr, Ge or Si): the change in unit cell dimension affects the structure of the TiO_5 unit, and affects the strength of the optical nonlinearity. Furthermore, crystalline phase which deposited from bulk glass phase must receive tensile stress since the difference of the density from that of surroundings ($d_{crystal} > d_{glass}$). So this stress can affects the dimension of the unit cell, namely the strength of optical nonlinearity.

The aim of this study is to clarify the relationship between the strength of optical nonlinearity and the crystal structure parameter by means of computational chemistry. Model clusters of TiO_5 unit and fresnoit-type crystals were constructed. The hyperpolarizability (β) values of the clusters were calculated using time dependent Hartree–Fock treatment with changing the dimension of the clusters.

2. Calculation

The clusters used were small one, $TiO_5H_4{}^{2-}$ to simulate the TiO_5 unit and larger ones, $Ba_8Ti_2Ge_8O_{34}H_{16}Sp_8$, $Ba_8Ti_2Si_8O_{34}H_{16}Sp_8$, and $Sr_8Ti_2Si_8O_{34}H_{16}Sp_8$ which are tandem structure of two unit cells to simulate BTG, BTS and STS,

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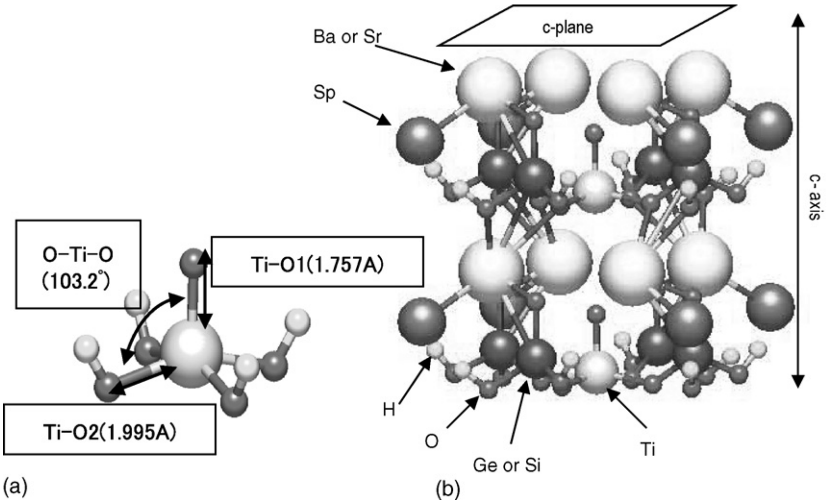

Fig. 1. Structures of the clusters. (a) $TiO_5H_4^{2-}$, (b) (Ba or Sr)$_8$Ti$_2$(Ge or Si)$_8$O$_{34}$H$_{16}$Sp$_8$. Sp is imaginary element which has charge −0.5 and no atomic orbital.

respectively (Fig. 1). Geometry of the small cluster was optimized in MO calculation. Those of larger ones were determined on the basis of X-ray diffraction data.[6–8] Sp is an imaginary element which has charge of −0.5 and has no atomic orbital. Sp was introduced as an alternative of corner shared oxygen atom to compensate the charge neutrality and the geometrical symmetry. H was used to avoid to make dangling bond and also to keep charge neutrality.

Hyperpolalizability (β) of the clusters were obtained through time dependent Hartree–Fock treatment[9] using rhf/6–31 + G* ab initio calculation on Gaussian03[10] for $TiO_5H_4^{2-}$ and through PM5 semiempirical calculation on MOPAC2002[11] for larger clusters.

Dimension of the clusters changed in axial direction (in *c*-axis direction) and in equatorial plane (in *c*-plane) independently.

3. Results and discussion

Fig. 2 shows the change of β value with the change of geometry parameters of $TiO_5H_4^{2-}$. β value increases both with expanding in axial direction (*c*-axis direction) and in equatorial plane (in *c*-plane).

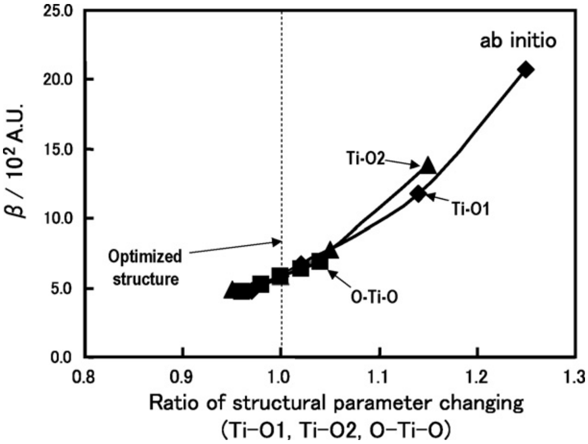

Fig. 2. β values of $TiO_5H_4^{2-}$ with geometry parameter change. Notation of Ti–O1, Ti–O2, and O–Ti–O corresponds to Fig. 1.

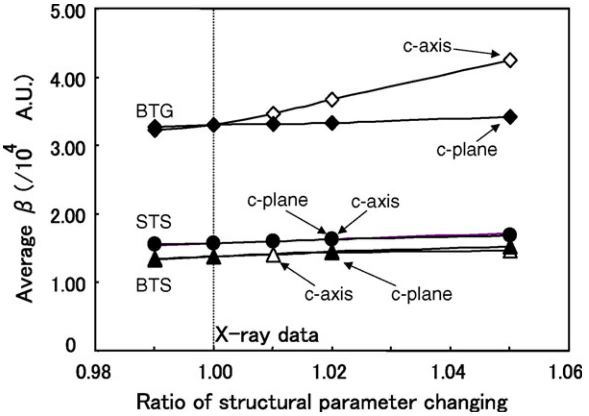

Fig. 3. β values of BTG, BTS and STS clusters with geometry parameter change.

Fig. 3 shows the change of β value with the change of geometry parameters of larger clusters (BTG, BTS, and STS). At the X-ray data structure (ratio = 1.0), β value of BTG is the largest and the values of BTS and STS were comparable. It is consistent with experimental results.[5] In all crystal clusters, β value increases both with expanding in axial direction (*c*-axis direction) and in equatorial plane (in *c*-plane). Especially, expansion in axial direction (*c*-axis direction) of BTG cluster caused remarkable increase in β value.

Both results in Figs. 2 and 3 suggest, the β value i.e. the strength of optical nonlinearity increase with the change of cell dimension under tensile stress.

4. Summary

Calculated optical nonlinearity of TiO_5 unit increased both with expansion in *c*-axis and in *c*-plane.

BTG cluster exhibited the largest β value in comparison with BTS and STS clusters. It is consistent with experimental results.

In all crystal clusters, β value increases both with expanding in c-axis direction and in c-plane. Especially, BTG showed significant increase of β value when the cluster was elongated in c-axis direction.

Above results suggest that fresnoit-type crystal is a potential material in which the strength of optical nonlinearity can be controlled artificially through distorting the crystal structure by applying external forces.

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