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Anisotropy optical properties of $KSr_2Nb_5O_{15}$ lead-free ferroelectrics: First-principle calculations

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ABSTRACT

The electronic and optical properties of $KSr_2Nb_5O_{15}$ (KSN) are investigated via first principle calculations along (100), (010), and (001) directions. The results show that KSN has a huge anisotropy in optical properties with a larger dielectric constant, reflectivity, refractive index and extinction coefficient at (001) direction than that at (100) and (010) directions, suggesting much easier transition of electrons at (001) direction. Dielectric function and conductivity calculation results verify that electronic transition mainly appears between Nb-4d and O-2p state. KSN is transparent in the range of 0–2.3 eV, while shows refractivity in the range of 2.5–5 eV and shows favorable reflectivity in the range of 3.6–7.8 eV. These theoretical insights into the microscopic intrinsic properties of KSN would provide fundament for further understanding KSN materials and broadening its application fields.

1. Introduction

$KSr_2Nb_5O_{15}$ (KSN) is a lead free ferroelectric material with obvious photorefractive effect, and it shows good electronic-optical properties similar with $Sr_{1-x}Ba_xNb_2O_6$ [1–3]. KSN single crystal shows 7 times electrooptical coefficient larger than that of $LiNbO_3$ at room temperature [4]. It also possesses high dielectric constant, which is a critical factor in oscillator and temperature compensation capacitor [5]. These excellent properties attract many researchers' attention to study on KSN.

KSN is a solid solution of $KNbO_3$-$SrNb_2O_6$ [4] with tetragonal tungsten bronze structure. Recently, KSN textured ceramics with grains grow along (001) direction and the preferred orientation has been fabricated using reactive template grain growth (RTGG) method [6], which showed anisotropy electrical properties along different lattice directions. E.A. Giess et al. found that KSN has much larger dielectric constants at direction paralleled to the tetragonal c axis than that at vertical direction [3]. Liu et al. reported that KSN shows different XRD patterns along parallel and vertical directions [7]. Because of its special symmetry of the lattice structure, the anisotropic optical properties of KSN are expected.

What is more, KSN can be potentially used in photocatalytic reactions under UV irradiation. Zhang et al. [8] reported that KSN has high photocatalytic activity in degradation of acid red G under UV irradiation, and the changes in the absorption spectra of 30 mg/L acid red G solution by 2.5 g/L catalyst at different reactions time were recorded by UV–vis spectrometer. Juan Matos studied the photochemical reactivity of apical oxygen in KSN materials under UV irradiation, which shows that the KSN samples were photoactive under UV irradiation and 4 times higher photocatalytic activity than the commercial TiO_2 [9]. However, these reports about optical properties were limited in the UV irradiation range and lack of explanation for optical mechanism in atomic scale. Therefore, it is necessary to study the optical properties in a larger frequency range - photon frequency by first principles calculation to give us an explanation of optical properties mechanism in atomic scale and dig more potential application of KSN. The first principle calculation has been successfully used for studying the photocatalytic activities, optical properties, electronic structures et al. of the tetragonal tungsten bronze materials, such as the $K_4R_2M_{10}O_{30}$ (R = Y, La, Ce, Nd, Sm; M = Ta, Nb) [10], $K_4Ce_2Ta_{10-x}O_{30}$ [11], $Ba_3Ta_5O_{14}N$ [12], $Ca_{0.4}Ba_{0.6}Nb_2O_6$ [13], $K_{3-x}Li_{2+x}Nb_5O_{15}$ [14] et al. For the ferroelectricity, the observed polarization may be switched in the presence of an external electric field. It is this “switchability” that is the basis for the technological relevance of ferroelectric materials. In the ferroelectricity study process, the origin and magnitude of the aforementioned functional properties are critically dependent on the individual asymmetric units as well as their alignment in the crystal structure. Therefore, applying first-principles is a good way

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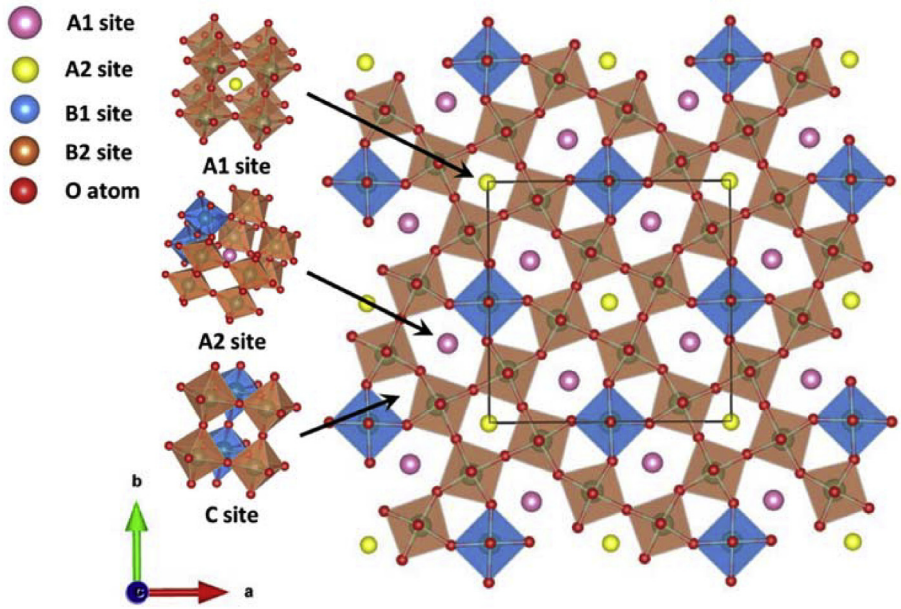

Fig. 1. Tetragonal tungsten bronze lattice structure.

to build an ideal model and predict the properties of ferroelectricity [15].

In this paper, first principles calculation is applied to calculate the electronic structure and optical properties along three different polarization directions (100), (010) and (001). The parameters including dielectric function, conductivity, refractive index, extinction coefficient, reflectivity, loss function and absorption coefficient were analyzed, as well as its anisotropic optical properties.

2. Calculation methods

Tungsten bronze lattice displays a tetragonal structure with a general formula of $(A1)_4$ $(A2)_2C_4(B)_{10}O_{30}$, typified by oxygen octahedral sharing their corners in a complex way to yield three types of openings: A (A1 and A2), B and C, as shown in Fig. 1. The A1 cavities have a cuboctahedral coordination of oxygen atoms, the A2 cavities are pentacapped pentagonal prismatic, and C cavities have tricapped trigonal prismatic coordination. The size of these cavities decreases in the order of A2 > A1 > C. The A sites are occupied by Sr^{2+}, Ba^{2+}, Ca^{2+}, K^+ or Na^+, the C sites by Li^+, and the B sites are filled with either Nb^{5+} or Ta^{5+} [5]. The polar unit is BO_6 octahedron, where the interaction between B atoms and the oxygen framework in the polar unit predominantly accounts for the ferroelectricity along c-axis [16–19].

All calculations are performed using CASTEP code. Structure optimization is performed within the framework of DFT (density functional theory) [20]. The interaction between ions and electrons is described by plane-wave pseudopotential due to its advantages in both efficiency and reliability. The exchange and correlation functions are treated within the generalized gradient approximation (GGA) with Perdew Wang 91 (PW91) and local density approximation (LDA) in the first optimization step. However, GGA and LDA calculation always underestimate the bandgap seriously, which will have a strong impact on the energy dispersion relation of materials and finally lead to mistake on the representation of optical properties. Fortunately, HSE06 hybrid function can avoid this problem and describe the bandgap and optical properties accurately [21], thus HSE06 hybrid function was employed to calculate the electric structure and optical properties of KSN [22].

Before performing the calculations, the convergence with respect to the cut-off energy and k-points have carefully been determined. The Kohn-Sham wave functions of valence electrons are expanded by a plane-wave basis set within a cut-off energy of 750 eV. The Monkhorst pack K-point mesh is set to 6×6×6 for structural optimizations, which are relaxed until the force on each atom is less than 0.03 eV/Å and an energy convergence criteria is 1.0×10^{-5} eV/Å for the gradient, as well as the residual bulk stress is 0.05 GPa. Because the calculation by HSE06 will cost much more time than LDA and GGA for the complex structure of KSN, the electric properties and optical properties with cutoff energy 600 eV and k-points 1 × 1 × 3 are used to decrease the calculation time. The states of Sr ($4s^24p^65s^2$), K ($3s^23p^64s^1$), Nb ($4s^24p^64d^45s^1$) and O ($2s^22p^4$) are treated as valence states.

3. Results and discussion

3.1. Structure characterization of KSN

In the KSN tetragonal tungsten structure, Sr^{2+} and K^+ occupy the same rhombohedral site with the same quantity, which form disordered solid solution structure. The disordered structure distribution feature makes it difficult to do calculations by using the first principle. Therefore, reasonable ordering is an effective way to build model. It is helpful to understand the relationship between microcosmic atom structure and physical characteristic of ferroelectric materials via adopting ordered structure model that can give more physical information. The ordered structure applied to calculate is shown in Fig. 2.

The calculated equilibrium lattice constants and volume of KSN within both GGA and LDA are shown in Table 1. For tetragonal phase, it can be seen that the lattice constants are in good agreement with experimental values. The fairly good agreement shows that the present calculation process is highly reliable. But it is found that lattice constants calculated by GGA are larger than LDA. The main reason may be that GGA has over-modified the results of LDA in ion crystals [24]. Thus, LDA is applied to conduct the first principle calculations due to its lattice constants match well to experiment values based on the data in Table 1 [25].

3.2. Electronic structure of KSN

The bonding nature of KSN is further characterized by calculating the partial density of states (PDOS) of K, Nb, O, Sr, and KSN and the band structures of KSN (see Fig. 3 and Fig. 4 for the corresponding results). The PDOS of each element is compared with that of KSN, and this comparison revels that the plot of the KSN PDOS can be divided