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Electronic structure and vibrational properties of $KRbAl_2B_2O_7$

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ABSTRACT

The physical properties of $KRbAl_2B_2O_7$ have been considered in comparison with those of $K_2Al_2B_2O_7$ and $Rb_2Al_2B_2O_7$. The vibrational parameters of $KRbAl_2B_2O_7$ have been measured by Raman spectroscopy as very similar to those of $K_2Al_2B_2O_7$. The electronic structures of $KRbAl_2B_2O_7$ have been evaluated by X-ray photoelectron spectroscopy and ab initio computations using CASTEP package. A noticeable refractive indices increase and small decrease of nonlinear optical properties have been found in $KRbAl_2B_2O_7$ in reference to optical parameters of $K_2Al_2B_2O_7$.

1. Introduction

Potassium aluminum borate $K_2Al_2B_2O_7$ (KABO), space group *P*321, is one from the best borate crystals applicable to optical frequency conversion in ultraviolet (UV) spectral range [1–5]. The structure of KABO is shown in Fig. 1, which clearly displays that the nearly planar ($Al_3O_3O_6$) networks perpendicular to the *c*-axis are connected to one another by bridged oxygen atoms and the alkaline cations (K^+) are located between the layers. In a ($Al_3O_3O_6$) unit, each Al^{3+} cation is linked with three terminal O atoms of the triangle $(BO_3)^{3-}$ groups and a bridged oxygen ion to form a tetrahedral $(AlO_4)^{5-}$ group. This structural feature indeed benefits to the generation of wide energy band gap ($E_g \sim 6.9$ eV) and moderate birefringence (∼0.07) in KABO [2,3]. Even higher value of E_g = 7.8-8.2 eV has been measured recently from iron-free KABO crystals [6,7]. In order to expand the applications in the optoelectronic devices, the ionic engineering is necessary to modify the vibrational, electronic and optical properties in KABO.

Wide-range element substitution is possible at K^+ and Al^{3+} sites in KABO crystal lattice and several compounds and solid solutions related to KABO family were observed in the past [8–12]. Recently, a solid solution $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ with as high upper limit at room temperature as $x \sim 0.75$ has been discovered [13]. However, only structural properties of $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ solid solutions were obtained in [13] for several compositions. Thus, the present study is aimed at the evaluation of vibrational properties and electronic structure of $KRbAl_2B_2O_7$ (KRABO) borate. Vibrational properties of KRABO will be studied by Raman spectroscopy in comparison with the earlier results obtained for KABO to see the effect of half-filling of K^+ sites by Rb^+ atoms in KABO-type crystal lattice [14]. The electronic structure is planned to be evaluated in parallel by experimental and theoretical methods. This algorithm is helpful for the selection of optimal approximation in band structure calculations and the prediction of optical properties of KRABO, as it was made earlier for several complex borate, sulfide and oxyfluoride crystals [15–22].

2. Experimental methods

A powder sample of $KRbAl_2B_2O_7$ was prepared by solid-state synthesis using a mixture of $Al(NO_3)_3{\cdot}9H_2O$ (pure), H_3BO_3 (chemically pure grade), K_2CO_3 (chemically pure grade), Rb_2CO_3 (chemically pure grade) in stoichiometric ratio as a starting material. A detailed description of the reaction route and thermal

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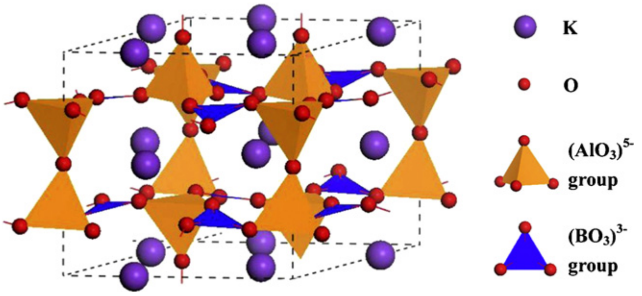

Fig. 1. Unit cell of $K_2Al_2B_2O_7$.

treatments was given elsewhere [13]. Phase purity of the final product was verified by XRD analysis. Micromorphology of the sample was observed by SEM using LEO 1430 device. Raman scattering experiment was carried out in quasi right angle scattering geometry with a triple grating spectrometer TriVista 777 under illumination by a line of λ = 532.1 nm of continuous solid-state laser Millenia (power 0.2 W) at room temperature. Wavelength scale calibration of the spectrometer was produced in reference to the spectrum of a neon-discharge lamp. The spectral resolution during measurements was $\sim$1.3 cm^{-1} (FWHM).

The electronic structure of $KRbAl_2B_2O_7$ was observed using surface analysis center SSC (Riber) with X-ray photoelectron spectroscopy (XPS) method. The nonmonochromatic Al Kα radiation (1486.6 eV), with the power source of 300 W, was used for the photoemission excitation. The energy resolution of the instrument was chosen to be 0.7 eV, so as to have a sufficiently small broadening of natural core level lines at a reasonable signal–noise ratio. Under the conditions the observed full width at a half maximum (FWHM) of the Au $4f_{7/2}$ line was 1.31 eV. The binding energy (BE) scale was calibrated in reference to Cu $3p_{3/2}$ (75.1 eV) and Cu $2p_{3/2}$ (932.7 eV) lines, assuring an accuracy of 0.1 eV in any peak energy position determination. Electronic parameters were defined for a fine KRABO powder gently pressed onto an In foil substrate. The photoelectron energy drift, due to charging effects, was taken into account in reference to the position of the C 1s (284.6 eV) line generated by adventitious carbon present on the surface of the powder as-inserted into the vacuum chamber. Chemical composition is defined using the detailed spectra of K $2p_{3/2}$, Rb 3d, Al 2p, O 1s and B 1s core levels and the known element sensitivity factors [23].

3. Computational methods

The calculations are based on the spin-polarized plane-wave pseudopotential (PWPP) method [24] implemented in the CASTEP package [25]. Normal-conserving pseudopotentials [26] are used with 1*s*, 2*s*, 2*p* electrons for potassium and aluminum and the 1*s* electrons for boron and oxygen treated as core electrons. For rubidium, the 4s, 4p and 5s electrons are treated as the valence electrons. A kinetic energy cutoff of 850 eV and the local density approximation are chosen for all the calculations. In order to investigate the influence of the ratio of K and Rb content on the structural, electronic and optical properties in the $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ compounds, we consider the following three simulated models: (i) $K_2Al_2B_2O_7$, (ii) $Rb_2Al_2B_2O_7$, and (iii) $K_1Rb_1Al_2B_2O_7$. Although the pure phase $Rb_2Al_2B_2O_7$ has not been obtained in experiments yet, the theoretical studies on the three representative compounds do provide the understanding on the evolution of the electronic structures and optical properties in these crystals as the alkaline metal cations are modified from K to Rb. Brillouin-zone integrations are made using $(3 \times 3 \times 4)$ *k*-point meshes according to the Monkhorst–Pack scheme [27]. The supercell volume and the atomic positions for the bulk are fully optimized using the quasi-Newton method [28]. The convergence thresholds between optimization cycles for energy change, maximum force, maximum stress, and maximum displacement are set as 10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively. The optimization terminates when all of these criteria are satisfied. Based on the optimized geometries, the electronic and optical properties are determined by the calculated methods developed earlier [16].

4. Results and discussion

4.1. Micromorphology, vibrational and core level properties

In Fig. 2 the micromorphology is shown for the sample with composition $K_{1.09(6)}Rb_{0.91(6)}Al_2B_2O_7$, space group *P*321, *a* = 8.6131(2), *c* = 8.5870(3) [13]. The powder is formed by irregular particles with dimensions in the range of $\sim$1-10 μm. The grains are well coalesced due to the interdiffusion activated by high temperature treatments during KRABO preparation. Pronounced dielectric properties of the sample are verified by strong surface charging effect during SEM measurements.

The unpolarized Raman spectrum of KRABO is shown in Fig. 3. More than 15 sharp lines are recorded for the powder sample and most strong scattering intensities are observed at 69.6, 342.1 and 1038.6 cm^{-1}, respectively. The total suite of Raman lines measured in KRABO is shown in Table 1. Generally, the Raman spectrum of KRABO is well related to that recorded earlier for KABO single crystal [14]. However, the lines at >1200 cm^{-1}, commonly related to BO_3 triangles in borate crystals, are of low intensity in KRABO spectrum [14,29–32]. It should be pointed that the effect of the frequency shift due to cation mass variation in the pair of KABO and KRABO is very small in comparison with that, for example, in a pair of $KTiOPO_4$ and $TlTiOPO_4$ [33].

The survey photoelectron spectrum recorded for KRABO, besides spectral features attributed to constituent element core levels and Auger lines, indicates the presence of several foreign lines. A line at 284.6 eV was attributed to C 1s signal related to adventitious hydrocarbons adsorbed on the surface. A line observed at 685.1 eV was related to F 1s signal that indicates an adsorption of fluorine from the laboratory atmosphere [34]. Furthermore, two lines at 444.0 and 451.7 eV were attributed to In 3d doublet generated by indium substrate. In Fig. 4 the Al 2p and O 1s lines are shown. The shape of Al 2p line is symmetrical and BE value is well related to individual valence state Al^{3+} in oxides [22,35,36]. As to the O 1s core level, an additive component at

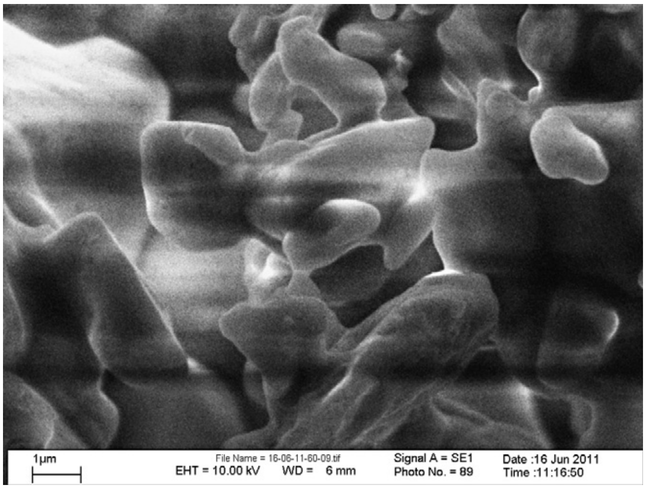

Fig. 2. SEM image of $KRbAl_2B_2O_7$ powder formed by solid state synthesis.