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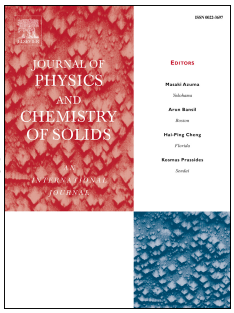

Structural, elastic, electronic and vibrational properties of a series of sulfates from first principles calculations

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Structural, elastic, electronic and vibrational properties of a series of sulfates from first principles calculations

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Abstract

The structural, elastic, electronic and vibrational properties of crystalline sulfates MSO_4 (M=Mg, Ca, Zn, Sr, Ba, Pb) were investigated within the framework of density functional theory using CRYSTAL program. The geometrical parameters, elastic constants and moduli, hardness, sound velocities, thermal conductivity, band gaps, densities of states, atomic charges and vibrational frequencies were computed. The computed structures are in good agreement with experimental ones if dispersion correction is taken into account. The unit cell volume and metal-oxygen distance almost linearly increase as the cationic radius increases. Compression anisotropy is shown to be more significant for magnesium sulfate and zinc sulfate; for them linear modulus is maximal along the shortest axis and along S-O bond, respectively. As the cationic radius increases, elastic moduli, hardness, sound velocities and thermal conductivity have a tendency to decrease. Low thermal conductivities reveal that sulfates can be used as thermal barrier coatings. It has been established that cationic charges and band gaps almost linearly decrease with increase of cationic electronegativity. Intra-anionic vibrational frequencies have a tendency to increase as electrostatic forces between cations and oxygens become stronger.

Keywords: Ab initio calculations, Crystal structure, Electronic structure, Elastic properties, Lattice dynamics

1. Introduction

Sulfates research is of particular interest both for Earth and materials science. There are over a hundred of sulfate minerals in nature including anhydrite ($CaSO_4$), celestite ($SrSO_4$), barite ($BaSO_4$), anglesite ($PbSO_4$). Metals sulfates MSO_4 (M: Mg, Ca, Sr, Ba, Zn, Pb) are widely and variously applied in different fields of industry. Magnesium sulfate is used as an additive in the construction of road bases and airfield pavements. It is also used for preparation of fire-resistant compounds for impregnation of various materials. Manganese or dysprosium-doped calcium sulfate crystals are used as thermoluminescent material [1]. Calcium sulfate can be used both in sensible and latent heat storage materials. Barium sulfate is used during production of refractory materials, in electrochemical industry for batteries manufacturing, and also as a radiopaque and catalytic material. Celestite may be used as an additive in pyrotechnics and ceramics [2], and as a solid lubricant in molds and engines as well [3]. Strontium, barium and lead sulfates are an attractive nonlinear optical material [4]. Lead sulfate has a wide range of applications in lead-acid batteries and as a pigments component. It has been widely used in scintillator material, electrode material for batteries and white dye [5, 6]. Zinc sulfate is used in production of mineral paints, glazes, in metallurgy, as well as in batteries and chemical sources of energy. Sulfates are mineral components of coal [7]. Moreover, sulfates are relevant to planetary science as well, since magnesium sulfate was found in sulfate sediments on Mars [8]. It is interesting to note that barium and calcium sulfates were found in meteorites [9].

Crystal structures of sulfates have been studied by neutron and X-ray diffraction [10-13]. The ambient phase of magnesium sulfate (Fig. 1) has an orthorhombic structure with space group *Cmcm* [10]. The magnesium cation in these structure is surrounded by 6 oxygen atoms. The S-O1 and S-O2 distances in sulfate anion differ by 0.043 Å. Anhydrite, $CaSO_4$, is one of the most common sulfate minerals in the earth's crust and occurs in the form of hydrothermal deposits on the seabed. It has an orthorhombic structure *Amma* (Fig. 1), consisting of eight coordinated Ca atoms and nearly perfect tetrahedra SO_4 [11].

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