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PHASE TRANSITION AND STRUCTURE OF $K_2Fe(SO_4)\cdot 4H_2O$

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In a Tutton's-salt like family with Fe atom, three compounds $K_2Fe(SO_4)\cdot nH_2O$ (n = 2, 4 or 6) are known. The phase transition in $K_2Fe(SO_4)\cdot 2H_2O$ was already examined by the authors' group. Anomalies of both specific heat and dielectric constant were recently found on the title compound at 283 K. Structure analyses were performed, therefore, at 303K (monoclinic, space group *C*2/*m*; a = 11.853(1), b = 9.544(1), c = 9.951(1) Å, β = 94.81(1)°, V = 1121.7(5)Å^3, Z = 4) and 123K (P21/a, Z=4). The cell dimensions showed no drastic changes above and below the transition temperature. The crystal consists of potassium cations and trans-$[Fe(SO_4)(H_2O)]$ complex anions which forms FeO_6 coordination octahedron through the O atoms. Two complex anions with similar geometry exist in the unit cell, which are chemically equivalent but crystallographically independent. The anion is highly symmetric in the high-temperature phase: the Fe atom occupies a center of inversion, and possesses a mirror plane through Fe, two S and four O (of SO_4) atoms together with a two-fold rotation axis bisecting the O(water)-Fe-O(water) angles. The anion loses the mirror and two-fold symmetries in the low-temperature phase. This transition feature differs from that of $K_2Fe(SO_4)\cdot 2H_2O$ in which large rotational changes of the H_2O molecules were observed along with the halved cell volume in the high-temperature phase.

Keywords: $K_2Fe(SO_4)_2\cdot 4H_2O$, PHASE TRANSITION, HYDROGEN BOND

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THE METAL-INSULATOR TRANSITION IN $Y_{1-X}Ca_XTiO_3$ CAUSED BY STRUCTURAL PHASE SEPARATION

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Perovskite-type Ti-oxide, $YTiO_3$, is well known as a Mott-Hubbard insulator with a d[1] configuration. It has been reported that Ca substitution for Y of this compound causes a metal-insulator (M-I) transition at around x=0.4 of $Y_{1-x}Ca_xTiO_3$. X=0.37 and 0.39 samples we prepared shows a first order type M-I transition at 60 K and 130 K, respectively. For x=0.41, the electrical resistivity measurement shows a metallic property from 1.5 K to 300 K. In order to understand the origin of the M-I transition, we have done the precise crystal structure analyses for x=0.37, 0.39 and 0.41 using the powder diffraction method by synchrotron radiation. The powder diffraction data of these materials were measured from 20 K to 300 K with intervals of 20K by using Large Debye-Scherrer Camera installed at BL02B2, SPring-8. The imaging plate was used as a detector to collect high counting statistics data. By the Rietveld analyses, the following aspects relating to the temperature dependence of the resistivity were found. For both x=0.37 and x=0.39, the orthorhombic (*P*bnm) to monoclinic ($P2_1/n$) phase transition occurs at around 230 K. The significant phase separation to monoclinic and low-temperature orthorhombic phases occurs in the vicinity of the M-I transition temperature for both x=0.37 and x=0.39. X=0.41 sample has already separated into two phases at room temperature. It was concluded from the structural information obtained in this study that the M-I transition was induced by not the structural phase transition but the phase separation. In addition, it was found that the low temperature orthorhombic phase contributed a metallic property.

Keywords: **METAL INSULATOR TRANSITION, PHASE SEPARATION, POWDER DIFFRACTION**

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POLYMORPHISM AND PROPERTIES OF THE DOPED $K_3NB_3B_2O_{12}$ CRYSTALS

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The $K_3Nb_3B_2O_{12}$ (KNB) single crystals attract much attention as new materials with complex polymorphism and unusual combination of antiferroelectric, ferroelectric, ferroelastic and superionic properties. The aim of the present work is investigation of the doping influence on the phase transitions and physical characteristics of these crystals. The KNB single crystals and their solid solutions with partial substitutions of K by Na or Rb, Nb by Ta or Sb, and B by Si were grown by flux method. Comprehensive study of the undoped KNB crystals have revealed 5 phase transitions in the temperature region from -100 to 600 Centigrade. The highest of them shows antiferroelectric properties (AFT), other transitions seem to have ferroelectric-ferroelastic nature (FFT). Symmetry of the high- temperature modification is hexagonal, the other phases have orthorhombic or more lower symmetry. Doping of KNB crystals by the above elements affects considerably the temperature of phase transition with the exception of Ta which leads only to strongly diffused phase transitions. Na-doping increases most of FFT temperatures more then by 200 centigrade that is accompanied by appearing of a new low-temperature phase transition while for the Rb, Sb and Si these temperatures drop. All impurities, espesially Sb, decrease AFT temperatures. Most of crystal properties (such as dielectric permittivity, piezoeffect) are highly anisotropic and have maximums along pseudohexagonal <0001> direction. KNB crystals and all of their solid solutions show high ionic conductivity in full temperature region and some of FFT are accompanied with superionic transitions.

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Keywords: **PHASE TRANSITIONS, FERROELECTRICS, SUPERIONIC CONDUCTORS**

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GROWTH AND PROPERTIES OF $KTiOPO_4$ CRYSTALS DOPED BY ANTIMONY

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$KTiOPO_4$ (KTP) and other crystals of this family are well known as excellent active elements for nonlinear optical applications. At the same time they are of a great scientific interest as representatives of a new specific type of solid-state materials: ferroelectrics-superionics. The present work deals with a physical properties of antimony-doped KTP crystals. The KTP crystals with the substitutions from 0.2 at.% to 27 at.% of Ti by Sb were grown by flux method from K_2O-TiO_2-Sb_2O_5-P_2O_5 system. The complex study of crystals included their chemical analysis, structural, dielectric, superionic and nonlinear investigations. The data obtained show that partial substitutions of tetravalent Ti ions by pentavalent Sb ones may be described by scheme $K_{1-x}Ti_{1-x}Sb_xOPO_4$ and chemical analysis supported the formation of additional vacancies in the potassium sublattice. Electrical conductivity KTP crystals doped by 2 at.% of Sb increases up to 1.5-2 orders of magnitude. The antimony doping was found to decrease significantly the ferroelectric phase transition temperature of KTP crystals. The concentration dependencies of the second harmonic generation intensity and of the Curie temperature have clearly defined nonlinear character. The antimony impurity gives rise to appearance of dielectric relaxor peak in temperature region 50 - 600 Centigrade. Its intensity is comparable with the ferroelectric phase transition peak intensity. Furthermore at 0.2 at.% Sb the additional maximums in relaxor peaks arise. This phenomena can be related with potassium vacancies. In some KTP crystals with small Sb content the phase transitions peaks can be split.

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Keywords: **KTP CRYSTALS, FERROELECTRICS-SUPERIONICS, PHASE TRANSITIONS**