DOI: 10.1002/ejic.201000124

Polymorphism of Fluoroargentates(II): Facile Collapse of a Layered Network of α-K_2AgF_4 Due to the Insufficient Size of the Potassium Cation

Dominik Kurzydłowski,*[a] Marianna Derzsi,[b] Armand Budzianowski,[b] Zvonko Jagličić,[c] Wiktor Koźmiński,[a] Zoran Mazej,[d] and Wojciech Grochala[a,b]

Dediacted to the memory of Neil Bartlett

Keywords: Silver / Fluorides / Polymorphism / Potassium

We report the crystal structure and magnetic properties of a novel β polymorph of K_2AgF_4. β-K_2AgF_4 is paramagnetic above 20 K and exhibits a low Curie temperature ($\theta < 5$ K). Solid state DFT (GGA and GGA+U) calculations were performed to analyze the electronic and magnetic structure of β-K_2AgF_4 at 0 K/0 GPa, reproducing correctly the ferromagnetic (FM) semiconductor ground state with the band gap at the Fermi level of approximately 1.65 eV. Furthermore, we show that the novel β form is thermodynamically favoured over the previously reported two-dimensional α form and can be formed either by slow spontaneous exothermic α to β phase transition occurring on heating or direct synthesis from KF and AgF_2 at 300 °C. The relative stability of the α and β phases is rationalized in terms of the size of the M^+ cation in the $M_2M'F_4$ series (M = Na, K, Cs, M′ = Cu, Ag) and the mismatch between [MF] and $[M'F_{4/2}]$ sublattices in the layered perovskite α form.

Introduction

Silver in the +2 oxidation state is a very strong oxidizer with an oxidation potential of +2.27 V in anhydrous HF,[1] which is why this cation is normally found in the environment of the most electronegative element, fluorine, while forming fluoroargentates(II). Despite their low resistance to atmospheric air and photosensitivity, this class of compounds is of particular interest as it exhibits many striking similarities to oxocuprates(II), which are precursors of the only known family of high-temperature superconductors (HTSCs).[2] These similarities have led to a claim that higher fluorides of silver may become precursors of a new family of HTSCs.[3]

A recent upsurge of interest in the chemistry of M^{n+}–Ag^{II}–F (M = metal) systems led to the observation of Meissner–Ochsenfeld anomalies in a Be–Ag^{II}–F ternary system.[4] McLain et al. revisited the structure and magnetic properties of Cs_2AgF_4,[5] and Mazej et al. determined the crystal structure of K_2AgF_4.[6] The structure of the layered polymorph (in this paper we will refer to it as to α-K_2AgF_4) consists of slightly puckered sheets of $[AgF_{2+4/2}]^{2-}$ stoichiometry with compressed octahedral coordination of the Ag^{II} centres. This 2D polytype of K_2AgF_4 exhibits FM ordering below 26 K.[6]

Herein we describe the preparation and structural characterization of a novel Na_2CuF_4-type[7] phase of K_2AgF_4 (hereafter referred to as β-K_2AgF_4) along with analysis of its electronic and magnetic properties. Formation of the new K_2AgF_4 phase is indicated by differential scanning calorimetry (DSC), thermogravimetry (TG) and ESR measurements, as well as far IR (FIR) and Raman spectroscopy and proved by powder XRD analysis. The β polymorph comprises chains of $[AgF_6]^{4-}$ octahedra and therefore is structurally and electronically one-dimensional, in contrast to recently characterized layered α-K_2AgF_4.[6] Our results indicate that the previously known α-K_2AgF_4 is in fact a metastable phase at ambient conditions, the novel β phase being the most thermodynamically stable form in these conditions.[8] We rationalize the relative stability of the two phases in terms of the size of the K^+ cation, which proves

---

[a] Faculty of Chemistry, University of Warsaw,
Pasteura 1, 02-093 Warsaw, Poland
Fax: +48-22-5540801
E-mail: dkurzydlowski@chem.uw.edu.pl
[b] Interdisciplinary Centre for Mathematical and Computational Modelling, University of Warsaw,
Pawińskiego 5A, 02-106 Warsaw, Poland
[c] Faculty of Civil and Geodetic Engineering and Institute of Mathematics, Physics and Mechanics, University of Ljubljana,
Jadranska 19, 1000 Ljubljana, Slovenia
[d] Department of Inorganic Chemistry and Technology, Jožef Stefan Institute,
Jamova 39, 1000 Ljubljana, Slovenia

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000124.

to be too small to stabilize the layered perovskite structure of α-K_2AgF_4. Ab initio DFT modelling reproduces the essential features of the electronic structure and magnetism of the β polymorph and gives insights into the relative stability of the α and β forms.

Results and Discussion

Phase Transition Between α and β-K_2AgF_4

The synthetic path for achieving K_2AgF_4 described in ref.[6] is a direct stoichiometric reaction between AgF_2 and KF (at 1:2 molar ratio) conducted at 480 °C. Violet α-K_2AgF_4 (*Cmca* space group, $Z = 4$) is obtained after annealing the product to room temp. We discovered[9] that if this compound is reheated to 180 °C and cooled down to room temp. again, it becomes grey.[10] The powder X-ray diffraction pattern (XRDP) of the sample quenched to room temp. is markedly different from that of α-K_2AgF_4, the reflexes of this phase being almost undetectable (Figure 1). The reflexes originating from the products of decomposition of K_2AgF_4 (i.e. KF, AgF and $K_3Ag_2F_7$) present in the XRDP are also very weak. All of the other peaks observed can be indexed with a monoclinic crystal structure ($P2_1/c$ space group). As the resulting cell vectors resemble those of the crystal structure of Na_2CuF_4[7] (see Supporting Information), we performed the refinement with a model structure of this type with K_2AgF_4 stoichiometry. The refinement yielded a polymorph denoted as β-K_2AgF_4. The XRDP of α-K_2AgF_4 reheated to 180 °C indicates that a phase transition from the α to β polytype must occur below this temperature. Indeed, simultaneous DSC and TG measurements of α-K_2AgF_4 point to a presence of an exothermic transformation below 190 °C[11] that is not accompanied by an appreciable loss of mass. This indicates that the observed exothermic heat transfer is not a result of the decomposition of α-K_2AgF_4 but rather originates from a spontaneous phase transition from a metastable polymorph (α-K_2AgF_4) to the thermodynamically more favoured one (β-K_2AgF_4). These results indicate that β-K_2AgF_4 is the ground state structure of K_2AgF_4 from room temp. up to at least 250 °C (the limiting temperature of our TG/DSC measurements, see Supporting Information), whereas α-K_2AgF_4 is a metastable polymorph in this temperature range. We subsequently discovered that β-K_2AgF_4 may also be obtained by direct synthesis from KF and AgF_2 (1:2 molar ratio) at 300 °C. However, the reaction is slow and needs two weeks to complete (compared to two days for the synthesis of α-K_2AgF_4 at 480 °C), which suggests slow kinetics of the formation of β-K_2AgF_4 from binary fluorides. The TG/DSC measurement conducted for β-K_2AgF_4 does not show any exothermic peaks below 250 °C, which shows that the transition from α- to β-K_2AgF_4 is irreversible, as expected for a transition from a metastable to a stable polytype (see Supporting Information).

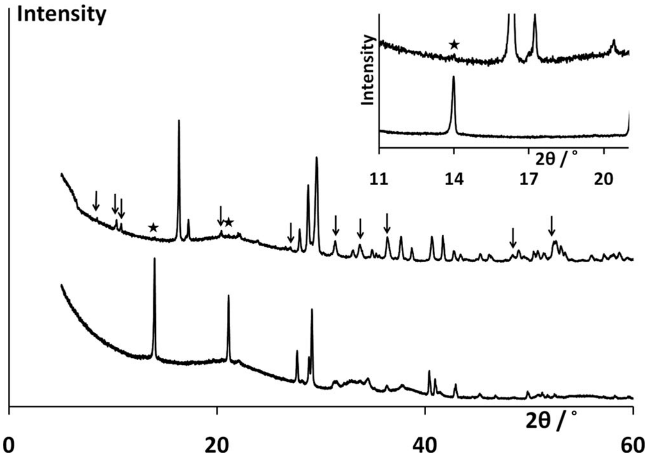

Figure 1. X-ray diffraction patterns (Cu-K_α radiation) of α-K_2AgF_4 (bottom) and the same compound heated to 180 °C for 2 h and cooled to room temp. (top). The changes in the X-ray profile result from a polymorphic transformation from α-K_2AgF_4 to β-K_2AgF_4. Arrows indicate the most intense reflexes from minority phases (KF, AgF, $K_3Ag_2F_7$ and an unidentified phase) present in β-K_2AgF_4. Stars mark signals from the residual α-K_2AgF_4 (inset).

DFT calculations at zero pressure and temperature (0 GPa, 0 K) show that the two phases of K_2AgF_4 are energetically almost degenerate, although the β phase is slightly favoured over the α phase by approximately 3 kJ/mol (this value is certainly smaller than the accuracy of the DFT methods: some 10 kJ/mol). Additionally, the volume of β is 3.0% smaller than that of α,[12] suggesting that the latter is indeed the high-temperature phase of K_2AgF_4 due to beneficial entropy factors.

Crystal Structure of β-K_2AgF_4

The two polymorphs of K_2AgF_4 differ substantially in terms of bonding topology and electronic dimensionality. Although Ag^{2+} adopts an octahedral coordination in both structures, α-K_2AgF_4 is characterized by a tetragonally compressed octahedron (2+4 coordination of Ag^{2+} by F^-), whereas the Na_2CuF_4-type structure exhibits a (2+2+2) distortion with a significant elongation of two Ag–F bonds (Figure 2). The α polymorph is two dimensional with puckered $[AgF_{2+4/2}]^{2-}$ sheets and corner-sharing octahedra, whereas β-K_2AgF_4 consists of chains of edge-sharing octahedra propagating along the crystallographic *a* axis (Figure 2). Large differences in bond lengths between the α and β polymorphs testify to the plasticity of the coordination sphere of Ag^{II},[13] similar to that found for analogous compounds of Cu^{II}.[14]

The coordination sphere of Ag^{2+} in β-K_2AgF_4, consisting of two very long Ag–F bonds (2.710 Å) and four shorter contacts (2 × 2.059 and 2 × 2.103 Å), can be viewed as nearly planar, similar to that of $Ag^{II}[MF_4]_2$ (M = Ag^{III}, Au^{III}).[15] The elongation of the $[AgF_6]^{4-}$ octahedra is confirmed by ESR measurements (see Supporting Information), which yield two *g* factors ($g_\parallel = 2.421$, $g_\perp = 2.100$) at 150 K. These values correspond well with *g* factors measured for other fluoroargentates(II) exhibiting elongated

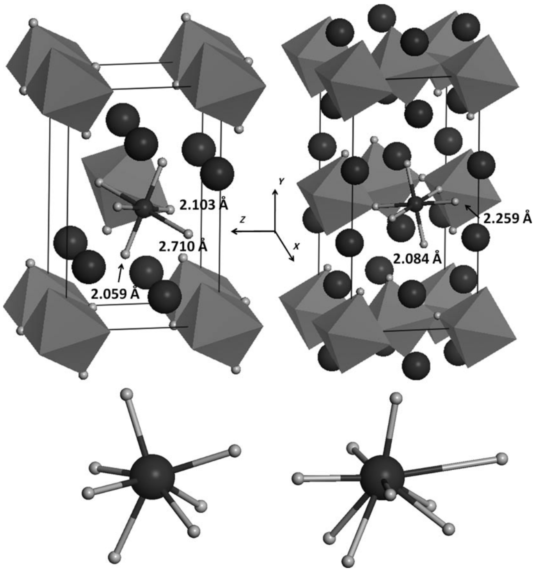

Figure 2. The room temp. crystal structures and coordination of K^+ cations for the β (left) and α (right) polymorphs of K_2AgF_4. Large and small dark balls represent the K and Ag atoms respectively, grey balls represent F atoms and $[AgF_6]^{4-}$ octahedra are marked in grey. The Ag–F bond lengths for both polymorphs are given for comparison.

$[AgF_6]^{4-}$ units, namely $KAgF_3$ ($g_\parallel = 2.425$, $g_\perp = 2.090$) and AgF_2 ($g_\parallel = 2.427$, $g_\perp = 2.122$).[6] The differences in bonding between the two polymorphs of K_2AgF_4 do not influence the ^{19}F NMR spectra of these compounds, which are nearly identical. They are, however, manifested in the broadening of the bands in the FIR spectra of β-K_2AgF_4 as compared to those of α-K_2AgF_4 (see Supporting Information for details concerning ^{19}F NMR, FIR and Raman spectra).

Magnetic and Electronic Properties of β-K_2AgF_4

Magnetic measurements reported by Mazej et al.[6] indicate that α-K_2AgF_4 orders ferromagnetically with a Curie temperature (θ) of 26 K.[16] The main interaction leading to magnetic ordering in this compound is the coupling of the unpaired spins within the $[AgF_{2+4/2}]^{2-}$ sheets with an intralayer magnetic coupling constant (J) of 4.5 meV. The FM ground state of α-K_2AgF_4 as well as the value of J have been nicely reproduced by the GGA+U calculations.[6] Magnetic measurements performed on the β-K_2AgF_4 sibling indicate paramagnetic behaviour of this compound down to approximately 5 K (Figure 3). At lower temperatures, an onset of a FM signal originating from β-K_2AgF_4 can be detected as seen in the χT vs. T dependence plot

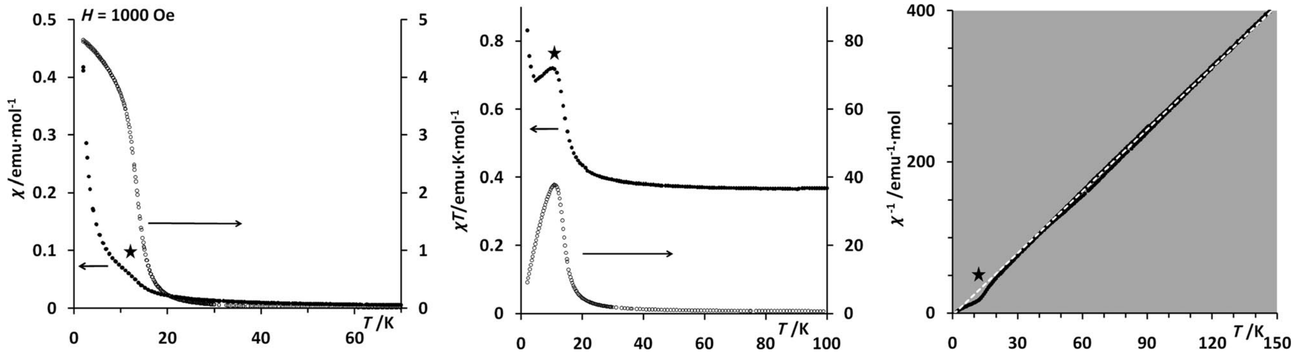

Figure 3. Magnetic susceptibility plots χ (left), χT (centre) and χ^{-1} (right) vs. temperature (T) for K_2AgF_4. Empty circles represent data for α-K_2AgF_4 (taken from ref.[6]) and full circles data for β-K_2AgF_4. Signals from the small α-K_2AgF_4 impurity are marked with a star. The white dotted line represents the fit of the χ^{-1} vs. T dependence (for $T > 50$ K) to the Curie–Weiss law. For hysteresis curves see Supporting Information (Figure S5).

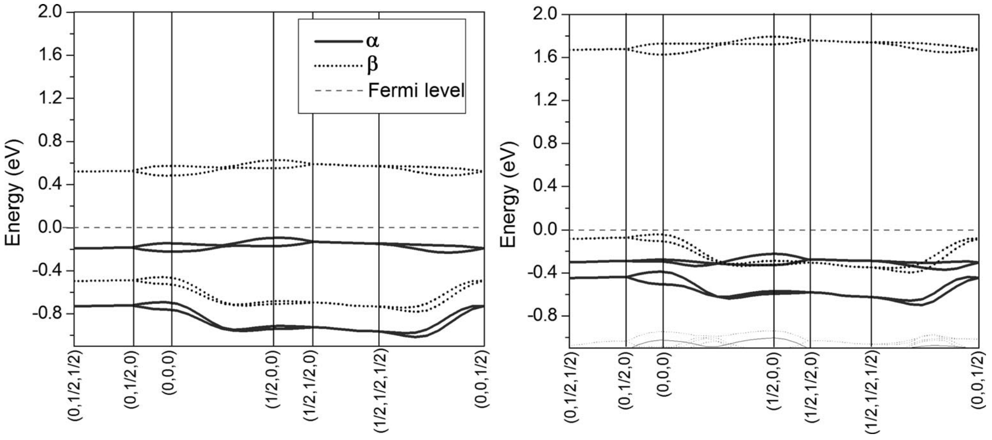

Figure 4. Electronic band structure near the Fermi level calculated for the FM ordered β-K_2AgF_4 at 0 K with spin-polarized GGA (left) and GGA+U methods (right) [$U_{Ag(d)} = U_{F(p)} = 4$ eV, $J = 1$].

(Figure 4). We observe another FM signal at higher temperatures ($T \approx 12$ K) which can be attributed to an α-K_2AgF_4 impurity present in our samples (Figure 3). The amount of this impurity does not exceed 5% by mass as determined from X-ray measurements (see Exp. Sect.). Therefore the paramagnetic signal observed in the high-temperature region ($T > 40$ K) originates mainly from the β polytype (the major phase). As α-K_2AgF_4 follows the Curie–Weiss law above approximately 40 K,[6] we fitted the magnetic data for $T > 50$ K and we obtained a positive value for θ of approximately 1 K. The derived Curie constant of 0.37 emu K mol^{-1} is in good agreement with the theoretical value for a system with one spin per formula unit (0.38 emu K mol^{-1} for $g = 2$). Although the value of the Curie temperature is certainly subject to an error (due to the presence of α-K_2AgF_4 impurities), it is clear that magnetic interactions in the Na_2CuF_4-type structure are much weaker than those in the α-polytype due to the 1D character of the former and 2D character of the latter. The fluoride bridges in the β polymorph are much longer (the length of the exchange pathway through Ag–F···Ag bonds is 4.812 Å) than those in the α polymorph (4.518 Å), which additionally weakens interactions between the electronic spins while leading to quasi-0D behaviour.[17]

In order to understand the nature of the FM ground state of β-K_2AgF_4 we conducted spin-polarized periodic DFT calculations on the GGA and GGA+U level of theory (see Exp. Sect. for details). Our results indicate that the lowest energy state indeed corresponds to FM ordering within the 1D $[AgF_{2+4/2}]^{2-}$ chains. The FM solution is favoured over the nonmagnetic (metallic) state to which AFM calculations have converged within both GGA and GGA+U frameworks. However, strong electron correlations induce a further and considerable stabilization of the FM state. While GGA favours the FM state over the metallic one by approximately 11 kJ/mol, the strong exchange (within the GGA+U framework) increases this energy difference to 44 kJ/mol.

Analysis of the electronic band structure calculated at the GGA level (Figure 4, left) shows that strong exchange does not play a crucial role for the band gap opening at the Fermi level. The gap of approximately 0.6 eV between two flat $4d_{Ag}/2p_F$ bands opens simply via orbital ordering. Thus, the case of β-K_2AgF_4 is different from that of its α-K_2AgF_4 sibling, where the exchange-driven mechanism of the gap opening is in operation.[6] An identical mechanism of the electronic band gap opening was observed for Cs_2AgF_4.[18] As both β-K_2AgF_4 and Cs_2AgF_4[5] exhibit an elongated octahedral (4+2) coordination of Ag^{II} with $[AgF_4]^{2-}$ units rather isolated from each other, the similarities in mechanism of the band gap opening come naturally despite many differences in the crystal structures of these compounds.

Inspection of the spin density of β-K_2AgF_4 shown in Figure 5 indicates that the unpaired electrons reside mostly on the $d(x^2–y^2)$ orbitals of Ag, which extend towards the four fluorine atoms closest to the silver atom (2 × 2.103 and 2 × 2.059 Å) forming a $[AgF_4]^{2-}$ plaquette. As expected, the $d(z^2)$ orbital, perpendicular to the plaquette, serves as a lone pair and carries no spin density. This finding corroborates the Jahn–Teller-effect-driven elongation of the $[AgF_6]^{4-}$ octahedra deduced from XRD and ESR experiments. Thus, the two lower bands (Figure 4, left), split by less than 0.3 eV, represent the filled $4d(z^2)$ orbitals, while the band gap opening results from the splitting (by ca. 0.56 eV) of the $4d(x^2–y^2)/2p(x,y)$ antibonding bands, with the spin minority states pushed above the Fermi level.

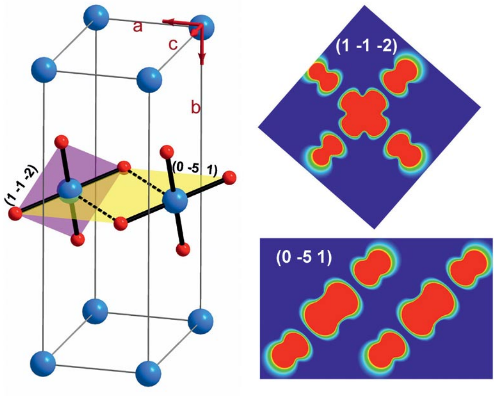

Figure 5. Crystal structure of β-K_2AgF_4 (showing only the Ag ions and mutual orientation of two $[AgF_4]^{2-}$ plaquettes) with two slices through the structure (left) and distribution of spin density around the Ag and F atoms within these slices (right). The excess spin density is marked in red. Projection in the (1 –1 –2) plane (top right) shows spin density within the $[AgF_4]^{2-}$ plaquette [one $4d_{Ag}(x^2–y^2)$ orbital mixed up with four 2p(F) ones]. Projection in the (0 –5 1) plane (bottom right), gives the top view of two such neighbouring $[AgF_4]^{2-}$ plaquettes lying perpendicular to the direction of propagation of 1D $[AgF_{2+4/2}]^{2-}$ chains.

The Influence of the Size of the M^+ Cation on the Crystal Structures of M_2CuF_4 and M_2AgF_4 Compounds (M = Na, K, Cs)

There are interesting similarities between the two families of M_2CuF_4 and M_2AgF_4 compounds, where M is an alkali metal. The crystal structures have only been solved for the copper(II) fluorides Na_2CuF_4[7] and K_2CuF_4.[19] The latter compound (a member of the Ruddlesden–Popper series) has a layered perovskite structure built up by corner-sharing $[CuF_6]^{4-}$ octahedra linked into flat $[CuF_{2+4/2}]^{2-}$ sheets. The elongation of the octahedra takes place in the basal plane, resulting in the alternation of the intrasheet Cu–F bonds. Substituting K^+ with smaller Na^+ (cubic ionic radii for K and Na are 1.65 and 1.32 Å, respectively) in K_2CuF_4 leads to considerable strain in the perovskite structure, which becomes unstable. As a consequence, Na_2CuF_4 exhibits chains of edge-sharing octahedra and may be viewed as a distorted Sr_2PbO_4 structure.[20]

In the case of the M_2AgF_4 series, only the structures of α-K_2AgF_4[6] and Cs_2AgF_4[5] have been previously determined. The Cs derivative is isostructural with K_2CuF_4 and has the same type of Jahn–Teller distortion. This could be expected as the ratio of the ionic radii[21] of Cu^{2+} and K^+

(r_{Cu}/r_K = 0.53) is similar to that calculated for Ag^{2+} and Cs^+ (r_{Ag}/r_{Cs} = 0.57). Structural features of Cs_2AgF_4 thus make it dissimilar to the La_2CuO_4-type structure[22] (adopted by many precursors of HTSCs) with its $[CuO_6]$ octahedra elongated in the direction perpendicular to the direction of propagation of the $[CuO_{2+4/2}]^{6-}$ sheets, here the two apical Cu–O bonds are longer than the equatorial bonds. One might reason that, to achieve the La_2CuO_4-type structure in the related M_2AgF_4 compounds, one should use a much more acidic (and therefore smaller) M^+ cation than Cs^+, potassium being an obvious choice. Unfortunately, changing from Cs^+ to K^+ in Cs_2AgF_4 results in a slight strain induced by the size mismatch between the [KF] and $[AgF_{2+4/2}]^{2-}$ sublattices, which in turn leads to the puckering of the $[AgF_{2+4/2}]^{2-}$ sheets as observed for α-K_2AgF_4. In other words, a small cation induces chemical pressure on the Ag/F sublattice, and as a consequence the $[AgF_6]^{4-}$ octahedra tilt about the *a* direction (Figure 2). This kind of distortion, however, releases the strain insufficiently, leading to a collapse of the layered α-type structure; the so-formed Na_2CuF_4-type (the β polymorph) is the lowest energy polymorph of K_2AgF_4 from room temp. up to at least 250 °C.[23] This result is not surprising for at least two reasons: (i) the ratio of ionic radii of Ag^{2+} and K^+ (r_{Ag}/r_K = 0.65) is nearly identical to that of Cu^{2+} and Na^+ (r_{Cu}/r_{Na} = 0.66) and (ii) the K^+ cation is significantly underbonded in the α polytype with nine close contacts between K and F atoms[24] (Figure 2), giving a bond valence sum of 0.88.[25] For the Na_2CuF_4-type structure (β phase), we find only seven contacts of this kind[24] (Figure 2), but the bond valence for K in β-K_2AgF_4 increases markedly to 1.06, leading to stronger bonding and improvement of thermodynamic stability. In conclusion, potassium cations are too small to stabilize the layered perovskite structure, and a structure with 1D chains of edge-sharing $[AgF_6]^{4-}$ octahedra is preferentially formed.

Conclusions

In this contribution we have structurally characterized a new polymorph of K_2AgF_4, the monoclinic semiconducting β phase of Na_2CuF_4-type structure. This novel phase has been characterized by DSC and TG measurements as well as by ESR, FIR and Raman spectroscopy. We have shown that the β polymorph, which can be obtained either by a phase transition from the α polytype or by direct reaction between AgF_2 and KF, is thermodynamically more stable than the previously characterized α form of K_2AgF_4 in the temperature range from room temp. up to at least 250 °C. The Na_2CuF_4 polytype is structurally very different from the layered α phase. It contains elongated $[AgF_6]^{4-}$ octahedra with quite isolated $[AgF_4]$ plaquettes arranged into quasi-one-dimensional chains. The consequence of its low structural dimensionality is that the magnetic exchange between the paramagnetic Ag^{2+} centres is weak, leading to ferromagnetic ordering only below several Kelvin with electronic band gap opening driven by magnetic ordering at 0 K.

Thermodynamic preference of β- over α-K_2AgF_4 results from the insufficient size of the potassium cation, which is too small to stabilize a layered network. One could speculate whether replacing K^+ with Rb^+ (between Cs^+ and K^+ in size) would improve the chance for obtaining a compound with (i) flat $[AgF_{2+4/2}]^{2-}$ sheets, (ii) no intrasheet bond length alternation and (iii) a long apical Ag–F distance. While the first two conditions might indeed be fulfilled by Rb_2AgF_4 (reported in 1974 by Odenthal et al.[26] but without structure determination), we feel that the third possibility is unlikely to be satisfied; the decreased acidity of Rb^+ as compared to K^+ would probably lead to shortening of the apical Ag–F bond similar to that observed for Cs_2AgF_4.[5]

Experimental Section

Synthesis

The synthesis of α-K_2AgF_4 was performed as described in ref.[6] The samples were handled in a glove box operating under an argon atmosphere with a water content not exceeding 1 ppm (Labmaster DP MBRAUN). All reaction vessels were made from PTFE (Teflon®). The synthesis of β-K_2AgF_4 was analogous to that of the α polytype, with the temperature of the furnace lowered to 300 °C and reaction time extended to two weeks (after annealing a 2KF/AgF_2 mixture at 300 °C for one day, only $KAgF_3$ is obtained together with unreacted substrates). The transformation from α to β phase of K_2AgF_4 was performed in an Ar atmosphere by heating α-K_2AgF_4 (placed in a PTFE vessel on a heating plate) typically for 1 h at 290 °C or for 2 h at 180 °C and subsequently cooling the sample to room temp. The amount of α-K_2AgF_4 used varied from 50 to 100 mg.

The first synthesis of β-K_2AgF_4 was completely accidental and occurred during the attempted synthesis of $KAgF_3$–$KZnF_3$ intergrowths[27] by using α-K_2AgF_4 and ZnF_2 as substrates.

Structure Solution from Powder Data

β-K_2AgF_4 was sealed in a 0.3 mm quartz capillary (Hilgenberg) in an argon atmosphere and characterized by powder X-ray diffraction (at room temp.) with a Bruker D8 Discover diffractometer. An 18 mm parallel beam from the Cu-K_α X-ray tube (λ = 1.5406 Å) was used to record diffractograms with a Vantec detector. The measurements were carried out in the range of 2θ from 7° to 120° with a 0.012° step (the counting time per step was 5795 seconds).

Structure refinement was performed on a β-K_2AgF_4 sample obtained from a phase transition at 290 °C, as it contained less impurities than that obtained at 180 °C or by direct synthesis at 300 °C. After initially indexing the strongest peaks present in the diffractogram, the Na_2CuF_4-type structure with K_2AgF_4 stoichiometry was chosen as the starting model (see Results and Discussion and Supporting Information). The refinement was preformed with TOPAS[28] software. We applied the Fundamental Parameters Approach[29] with the parameters of additional convolution for the instrument refined using a sample of silicone standard.

Refinement was performed for a multicomponent mixture of β-K_2AgF_4, α-K_2AgF_4, AgF and KF, for which the mass percentages of phases are 75.0%, 4.4%, 7.7% and 12.9%, respectively, and the R_B parameters for the particular phases are 0.619%, 0.891%, 0.172% and 0.634%, respectively. $R_B = \sum|I_{o,k} - I_{c,k}|/\sum I_{o,k}$, where $I_{o,k}$ and $I_{c,k}$ are the observed and calculated intensities of the k^{th} reflection. The overall R_{exp} and R_{wp} indices were 1.77% and 2.81%, respectively (for more details see Table S3 in the Supporting Information).

β-K_2AgF_4 crystallizes in a monoclinic ($P2_1/c$) Na_2CuF_4-type structure with a = 3.7174(1) Å, b = 10.2736(2) Å, c = 6.3856(1) Å and β = 91.744(1)° [Z = 2, V = 243.76(1) Å^3]. Its crystal structure consists of edge-sharing elongated $[AgF_6]^{4-}$ octahedra arranged into infinite one-dimensional $[AgF_{2+4/2}]^{2-}$ chains separated from one another by potassium cations.

Magnetic Measurements: Magnetic measurements were performed by using a Quantum Design MPMS-XL–5 SQUID magnetometer equipped with a 5 T superconducting magnet. The temperature dependence of susceptibility was measured between 2 and 300 K in a magnetic field of 1000 Oe, and magnetization was measured as a function of the magnetic field at 5 K. Data have been corrected for a contribution of an empty sample holder as well as for temperature-independent diamagnetism of inner shell electrons.

Computational Details

Solid-state Density Functional Theory (DFT) calculations were performed with ICM supercomputers using the VASP code[30] with the projector-augmented wave method (PAW)[31] as implemented in the MedeA package. For the exchange-correlation part of the Hamiltonian, the generalized gradient approximation (GGA)[32] was applied. During the full geometry optimization (cell and atomic parameters), the ionic relaxation was continued until the forces on individual atoms were less than 0.002 eV/Å. The electronic iterations convergence was set to 10^{-7} eV by using the standard blocked Davidson algorithm and reciprocal space projection operators. The spacing between the k-points for the k-points mesh generation was ca. 0.5 Å^{-1}. The valence electrons were described by plane waves with the kinetic energy cutoff increased from the standard value of 600 eV to 800 eV.

The spin-polarized GGA and GGA+U single-point calculations were performed on an experimental unit cell in order to reproduce the electronic and magnetic structure of β-K_2AgF_4 correctly. To mimic the strongly correlated nature of the d electrons of Ag and the interacting p electrons of the fluoride anions (within the superexchange Ag–F–Ag path), the value of the Coulomb integral U was set to 4 eV and Hund's exchange J to 1 eV for both of these ions. The calculations were done for both FM and AFM models, the latter converging spontaneously to a nonmagnetic (metallic) state. The values of magnetic moments on Ag, F1 and F2 atoms as obtained from the FM GGA+U calculations are 0.59 μ_B, 0.11 μ_B and 0.10 μ_B, respectively.

Supporting Information (see footnote on the first page of this article): TGA/DSC, ESR, Raman, FIR, ^{19}F NMR and magnetic hysteresis measurements for β-K_2AgF_4; comparison of experimental and calculated XRDP for β-K_2AgF_4; comparison of the colours of the two polymorphs; FIR and Raman frequencies for α and β polymorphs; the geometry of the structures optimized by the ab initio method (DFT); the details of Rietveld refinement for β-K_2AgF_4.

Acknowledgments

The project "Quest for superconductivity in crystal-engineered higher fluorides of silver" is operated within the Foundation for Polish Science "TEAM" Programme co-financed by the EU European Regional Development Fund. This work has been partly supported by the Slovenian Research Agency (ARRS) within the research program P1-0045 Inorganic Chemistry and Technology, W. G. would like to thank the Faculty of Chemistry and Interdisciplinary Centre for Mathematical and Computational Modelling (ICM), University of Warsaw, for continuing sustenance.

---

[1] W. Grochala, *J. Fluorine Chem.* **2008**, *129*, 82–90.

[2] W. Grochala, *J. Mater. Chem.* **2009**, *19*, 6949–6968.

[3] W. Grochala, R. Hoffmann, *Angew. Chem. Int. Ed.* **2001**, *40*, 2743–2781.

[4] W. Grochala, A. Porch, P. P. Edwards, *Solid State Commun.* **2004**, *130*, 137–142.

[5] S. E. McLain, M. R. Dolgos, D. A. Tennant, J. F. C. Turner, T. Barnes, T. Proffen, B. C. Sales, R. I. Bewley, *Nat. Mater.* **2006**, *5*, 561–566.

[6] Z. Mazej, E. Goreshnik, Z. Jagličić, B. Gaweł, W. Łasocha, D. Grzybowska, T. Jaroń, D. Kurzydłowski, P. Malinowski, W. Koźmiński, J. Szydłowska, P. Leszczyński, W. Grochala, *CrystEngComm* **2009**, *11*, 1702–1710.

[7] D. Babel, *Z. Anorg. Allg. Chem.* **1965**, *336*, 200–206.

[8] Preliminary results were presented during the *19th International Symposium on Fluorine Chemistry*, Jakson Hole, WY, USA, 23–28 August, **2009**.

[9] This discovery was entirely accidental, as we originally attempted to generate the [$KAgF_3$–$KZnF_3$] intergrowth from the α-K_2AgF_4 and ZnF_2 reagents.

[10] See Supporting Information for photos of the two phases.

[11] The temperature of the transition depends on the parameters of the TG/DSC experiment; for a discussion see Supporting Information.

[12] As the structure of the α polytype was determined at 200 K (ref.[9]) and that of the β polymorph at room temp., the difference in room temp. volumes between α and β-K_2AgF_4 must be even larger.

[13] W. Grochala, *Phys. Status Solidi B* **2006**, *243*, R81–R83.

[14] J. Gažo, I. B. Bersuker, J. Garaj, M. Krabešová, J. Kohout, H. Langfelderová, M. Melník, M. Serátor, F. Valach, *Coord. Chem. Rev.* **1976**, *19*, 253–297.

[15] O. Graudejus, A. P. Wilkinson, N. Bartlett, *Inorg. Chem.* **2000**, *39*, 1545–1548.

[16] The paramagnetic Curie temperature (θ) taken from the Curie–Weiss law may generally differ from the temperature of the ferromagnetic ordering (T_C). This is the case for α-K_2AgF_4, Cs_2AgF_4 (ref.[9]) and K_2CuF_4 (ref.[20]) for which $T_C < \theta$.

[17] Interestingly, the intrachain Ag···Ag contacts (3.72 Å) in β-K_2AgF_4 are much shorter than intrasheet contacts in α-K_2AgF_4 (4.46 Å).

[18] M. Kasinathan, K. Koepernik, U. Nitzsche, H. Rosner, *Phys. Rev. Lett.* **2007**, *99*, 247210–1–247210–4.

[19] M. Hidaka, K. Inoue, I. Yamada, P. J. Walker, *Physica B* **1983**, *121*, 343–350; I. Yamada, *J. Phys. Soc. Jpn.* **1972**, *33*, 979–988.

[20] M. Troemel, *Z. Anorg. Allg. Chem.* **1969**, *371*, 23–247.

[21] Octahedral Shannon–Prewitt ionic radii for Cu^{2+} and Ag^{2+} and cubical ionic radii for Cs^+, K^+ and Na^+ were taken from: http://www.webelements.com accessed on Jan 15, **2009**.

[22] P. G. Radaelli, D. G. Hinks, A. W. Mitchell, B. A. Hunter, J. L. Wagner, B. Dabrowski, K. G. Vandervoort, H. K. Viswanathan, J. D. Jorgensen, *Phys. Rev. B* **1994**, *49*, 4163–4175.

[23] A possible low-temperature polymorphism of K_2AgF_4 has not been investigated as part of this work.

[24] For K···F distances shorter than the sum of van der Waals radii of K and F (4.22 Å): For α-K_2AgF_4 (9 contacts): 2.538, 2.656, 2 × 2.737, 2 × 3.046, 2 × 3.116, 3.800 Å; for β-K_2AgF_4 (7 contacts): 2.606, 2.622, 2.654, 2.668, 2.711, 2.752, 2.881 Å.

[25] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

[26] R. H. Odenthal, D. Paus, R. Hoppe, *Z. Anorg. Allg. Chem.* **1974**, *407*, 144–155.

[27] By analogy to the known $K_2(Cu,Zn)F_4$ series: Y. Fukada, M. Totani, I. Yamada, *J. Phys.: Condens. Matter* **1991**, *3*, 6925–6933; P. J. Walker, *Cryst. Growth* **1979**, *46*, 709–7190.

[28] Bruker AXS *(2009): TOPAS 4.2* User manual, Bruker AXS GmbH, Karlsruhe, Germany, **2009**.

[29] J. Bergmann, R. Kleeberg, A. Haase, B. Breidenstein, *Mater. Sci. Forum* **2000**, *347–349*, 303–308.

[30] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.

[31] P. E. Blöch, *Phys. Rev. B* **1994**, *50*, 17953–17979.

[32] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

Received: February 3, 2010