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On a Low-Temperature Form of $KBiF_4$

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The existence of a low-temperature α form of $KBiF_4$ has been shown by differential thermal analysis and microcalorimetry as well as by electrical measurements. Properties of α-$KBiF_4$ are compared to those of $K_{1-x}Bi_xF_{2x+1}$ ($0.50 \leq x \leq 0.70$) with fluorite-type structure and KBi_3F_{10}.

Many phases with high ionic conductivity have been isolated in the MF–BiF_3 (M = Na, K, Rb, Tl) systems (*1–3*). Neutron diffraction studies have shown that the materials with the best electrical performance are characterized by high anionic disordering (*4*). For instance for the $K_{1-x}Bi_xF_{2x+1}$ solid solution ($0.50 \leq x \leq 0.70$ at 450°C) the highest mobility is observed for $KBiF_4$ (ΔE = 0.38 eV), which can actually be formulated $K_{0.50}Bi_{0.50}(F_I)_{1.50}(F'_{II})_{0.50}(V_{F_I})_{0.50}$ (where F_I and F'_{II} are respectively normal and interstitial anions and V_{F_I} represents normal site vacancies). An increasing content of Bi^{3+} in $K_{1-x}Bi_xF_{2x+1}$ ($x > 0.50$) decreases the mobility because of the trapping effect of the supernumerary Bi^{3+} cations. With rising x, ΔE increases linearly from 0.38 eV (x = 0.50) to 0.48 eV (x = 0.70). For KBi_3F_{10} with definite composition, which has an ordered KY_3F_{10} structure (*5*), ΔE is as high as 0.53 eV (*2, 4*).

This article is devoted to a thermal and electrical investigation of $KBiF_4$. The material has been prepared by synthesis at 450°C from the binary fluorides KF and BiF_3 in a sealed gold tube. The X-ray pattern of the phase quenched from 450°C is characteristic of a fluorite-type structure; we shall call it β-$KBiF_4$. As a matter of fact, weak supplementary lines appear in the X-ray patterns when quenching is not sufficiently rapid. So far their origin has not been explained and perhaps this is the reason why the existence of stoichiometric $KBiF_4$ with the fluorite-type structure has been previously contested by M. W. Shafer *et al.* (*6, 7*).

The possible existence of a low-temperature form of $KBiF_4$ prompted us to an investigation by DTA and microcalorimetry as well as by electrical measurements. Low-temperature forms have been often detected in fact for fast ionic conductors, e.g., LuF_3 (*8*), AgI (*9*), or $PbSnF_4$ (*10*).

I. Synthesis of α-$KBiF_4$

A 1-week annealing of β-$KBiF_4$ at 290°C produced the low-temperature α-form of $KBiF_4$. α-$KBiF_4$ has been obtained by applying a high pressure (60 kbar) to β-$KBiF_4$ for 30 min at 290°C. In addition, we have been able to prepare α-$KBiF_4$ by direct syn-

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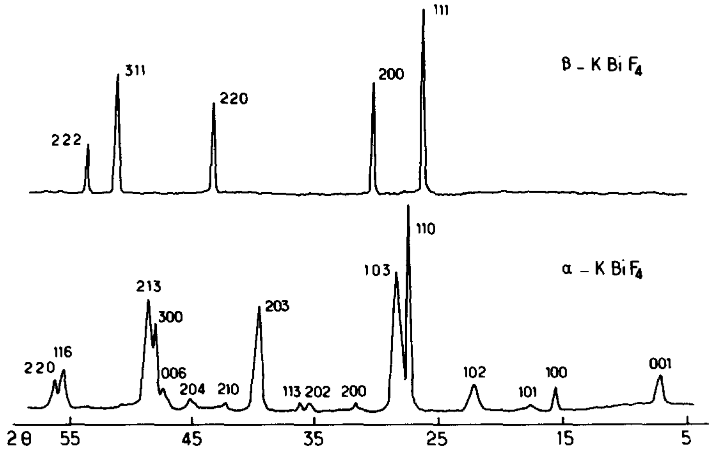

FIG. 1. X-Ray patterns of α- and β-$KBiF_4$.

thesis from KF and BiF_3 in a sealed gold tube at 290°C, but the reaction is only complete after 5 days heating.

The obvious analogy with the X-ray diffraction spectrum of $NaBiF_4$ (*11*) which is of the $NaNdF_4$-type structure (*12*) allowed

TABLE I

PARAMETERS AND COMPARATIVE INDEXATIONS OF α-$KBiF_4$ AND $NaNdF_4$

	α-$KBiF_4$ $a' = 6.530 \pm 0.004$ Å $c' = 11.445 \pm 0.008$ Å			$NaNdF_4$ $a = 6.100 \pm 0.003$ Å $c = 3.711 \pm 0.003$ Å (*12*)		
hkl	d_{calc} (Å)	d_{obs} (Å)	I/I_0	*hkl*	d_{calc} (Å)	I/I_0
001	11.4	11.7	15			
100	5.65	5.66	15	100	5.28	60
101	5.07	5.03	<5			
102	4.02	4.03	15			
110	3.265	3.268	100	110	3.050	100
103	3.163	3.176	60	101	3.037	90
200	2.828	2.831	<5	200	2.641	10
202	2.535	2.530	5			
113	2.481	2.486	5	111	2.356	10
203	2.272	2.275	45	201	2.152	70
210	2.138	2.140	5	210	1.997	10
204	2.011	2.002	5			
006	1.908	1.914	10	002	1.855	15
300	1.885	1.886	40	300	1.761	35
213	1.865	1.866	50	211	1.758	60
116	1.647	1.649	20	112	1.585	15
220	1.633	1.634	15	220	1.525	15
312	1.513	1.513	<5			
305	1.455	1.452	<5			
306	1.341	1.342	<5	302	1.277	5
403	1.326	1.326	<5	401	1.244	5

us to index the main lines of the α-$KBiF_4$ spectrum in a hexagonal system (Fig. 1). But the presence of supernumerary lines led us to consider a multiple cell of $NaNdF_4$: $a'_{hex} = a_{hex}$ and $c'_{hex} = 3c_{hex}$. Table I shows the comparative indexing of $NaNdF_4$ and α-$KBiF_4$ as well as the respective parameters. The measured density ($\rho_{exp} = 5.64 \pm 0.05$ g/cm^3) involves 9/2 formula units per unit cell ($\rho_{calc} = 5.74$ g/cm^3).

We have shown previously that $NaBiF_4$ has like $NaNdF_4$ a partially ordered structure with the following distribution of Na and Bi atoms: Bi (1a); $\frac{1}{2}$ Na, $\frac{1}{2}$ Bi (1f); Na, □ (2h). The existence for α-$KBiF_4$ of a multiple cell involves for this material supplementary ordering between planes perpendicular to the c axis.

II. DTA Study of α-$KBiF_4$

A DTA study of α-$KBiF_4$ has been performed on samples sealed in gold tubes under an argon atmosphere. The temperature variation is given in Fig. 2. With rising temperature we observe an endothermal peak at 315 ± 5°C which seems to characterize a first-order transition and a second peak at 630 ± 10°C which corresponds to the melting point of $KBiF_4$. The nonlinear baseline of the DTA pattern might be explained by a drastic change in C_p.

When the temperature decreases only a solidification peak is observed. However, if the melting point is not reached, the first-order transition peak appears on cooling, but with a weaker intensity. A 72-hr annealing of $KBiF_4$ at 290°C regenerates the transition peak with increasing temperature with its initial intensity. This phenomenon shows that the reversibility of the allotropic transformation α-$KBiF_4 \rightleftarrows \beta$-$KBiF_4$ is sluggish. An analogous observation was made on $PbSnF_4$ (*10*).

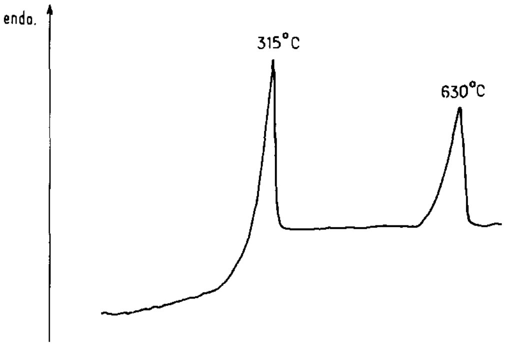

FIG. 2. DTA diagram of $KBiF_4$.

III. Microcalorimetry of α-$KBiF_4$

A microcalorimetric study of α-$KBiF_4$ has been carried out under the same conditions as the DTA study. It has allowed us to confirm the DTA results and to determine the heats of transition and melting as well as the entropy changes associated to them (Table II).

The corresponding values for several well-known solid electrolytes are enclosed for comparison in Table II. Like those materials, $KBiF_4$ exhibits an entropy change associated with the phase transition that is significantly greater than that corresponding to melting. This suggests that the high-temperature form might be highly disordered, a result which has been confirmed by neutron diffraction (*4*). This result supports the "liquid like" description of the mobility previously proposed by O'Keeffe and Hyde (*17*).

The two last columns of Table II give the sum of the entropies of transition and fusion per mole ($\Sigma\Delta S_1$) and per gram-ion ($\Sigma\Delta S_2$). $\Sigma\Delta S_2$ calculated for AgI, PbF_2, LuF_3, and YF_3 is close to the entropy of fusion of usual salts (KCl, $MgCl_2$, . . .): $\Delta S_m \simeq 11$ J K^{-1} per gram-ion (*13*, *18*). $\Sigma\Delta S_2$ obtained for $KBiF_4$ ($\Sigma\Delta S_2 \simeq 7.1$ J K^{-1} per gram-ion) is slightly weaker; it might be explained by a supplementary entropic term bound to the C_p variation accounting for the nonlinearity of the DTA baseline.

Specific heat measurements of $KBiF_4$ might confirm this hypothesis.

TABLE II

THERMODYNAMIC DATA RELATIVE TO OBSERVED PHASE TRANSITIONS EITHER WITHIN SOLID STATE OR AT MELTING TEMPERATURE

	$T_{tr.}$ (K)	$\Delta H_{tr.}$ (kJ/mole)	$\Delta S_{tr.}$ (J/deg · mole)	T_m (K)	ΔH_m (kJ/mole)	ΔS_m (J/deg · mole)	$\Sigma\Delta S_1$ (J/deg · mole)	$\Sigma\Delta S_2$ (J/deg · gram-ion)
AgI (13)	419	6.1	14.5	830	9.4	11.3	25.8	12.9
PbF_2 (14)	700	11.6	16.5	1098	18	16.4	32.9	11
LuF_3 (15)	1230	25.1	20.4	1457	30.3	20.8	41.2	10.3
YF_3 (15)	1350	32.4	24.0	1428	27.9	19.6	43.6	10.9
$BaCl_2$ (16)	1193	17.2	14.4	1233	16.3	13.2	27.6	9.2
$SrBr_2$ (16)	918	12.1	13.2	930	10.5	11.2	24.4	8.1
$KBiF_4$	588	15.1	25.7	903	15.2	16.8	42.5	7.1

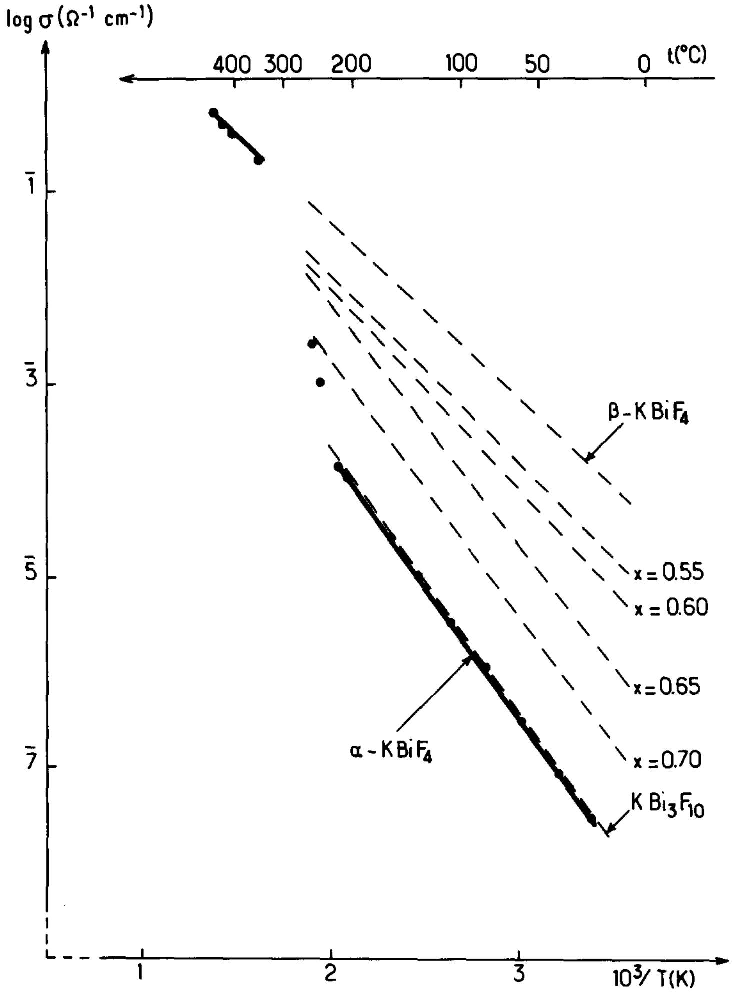

FIG. 3. Variation of log σ with reciprocal temperature for α-$KBiF_4$, β-$KBiF_4$, $K_{1-x}Bi_xF_{2x+1}$ (with x = 0.55, 0.60, 0.65, 0.70) and KBi_3F_{10}.

IV. Ionic Conductivity

Ionic conductivity measurements have been carried out on pellets of α-$KBiF_4$ obtained by annealing β-$KBiF_4$ pellets (prepared by sintering at 450°C) at 290°C for 72 hr. The bulk resistance has been determined by the complex impedance method using a "Solartron 1170" frequency response analyzer (*19*). The frequency range used is 5–10 kHz and measurements are carried out between 25 and 450°C. The conductivity variation as a function of temperature is given for α-$KBiF_4$ in Fig. 3. We have also reported in Fig. 3 the temperature dependence of the conductivity for a few β-type $K_{1-x}Bi_xF_{2x+1}$ ($0.50 \leq x \leq 0.70$) samples with fluorite type structure and for KBi_3F_{10}.

The electrical properties of α-$KBiF_4$ are very close to those of KBi_3F_{10} which is isostructural with KY_3F_{10}, whose structure is ordered (*5*).

When the temperature reaches that of the $\alpha \rightleftarrows \beta$ transition (315 ± 5°C), the beginning of an electrical transition is observed. At higher temperatures ($350°C < t < 450°C$), the experimental points fall into line with those previously obtained for β-$KBiF_4$ at lower temperatures. At the $\alpha \rightleftarrows \beta$ transition, a modification of the electrical properties is observed as previously noted for LuF_3 (*8*) or AgI (*9*).

β-$KBiF_4$ which shows the highest disorder has the best electrical performances. Replacement of potassium by bismuth in $KBiF_4$ produces a reduction of the conductivity for the $K_{1-x}Bi_xF_{2x+1}$ solid solution. This results from the progressive formation of isolated BiF_8 antiprisms and the onset of ordering between K and Bi atoms on one hand and elementary F_8 cubes and F_{12} cubooctahedra on the other hand (*4*). This local order becomes a long range one with increasing *x*, and is well established for KBi_3F_{10} which is the least performing material (*2*). In the same way, a long annealing of β-$KBiF_4$ at 290°C brings about a transformation of β-$KBiF_4$ into α-$KBiF_4$ which is an ordered phase. As a result α-$KBiF_4$ shows an important decrease of electrical performances.

As pointed out previously, a neutron diffraction study of β-$KBiF_4$ has shown that the material can be formulated $K_{0.50}Bi_{0.50}(F_I)_{1.50}(F'_{II})_{0.50}(V_{F_I})_{0.50}$ where F_I and F'_{II} are respectively normal and interstitial anions and V_{F_I} normal vacancies (*4*). As a consequence β-$KBiF_4$ has a fluorite-type structure relatively distinct from ideal CaF_2.

The tendency of bismuth to give a lone pair might be the origin of the metastability of β-$KBiF_4$, whose transformation is, in any case, favored by such a nonsymmetrical formulation. A similar behavior has been observed for β-PbF_2.

Acknowledgment

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