New Anionic Conductor $KSbF_4$ with Fluorite Structure

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A new fluoride ion conductor, β-form of $KSbF_4$, was synthesized and characterized by the conductivity, DTA, XRD, and ^{19}F NMR measurements. The low temperature modification, α-form, showed an irreversible phase transition at 455 K accompanied by a steep increase in conductivity. This high temperature modification was stable on cooling and belongs to a cubic system above 420 K with a disordered fluorite structure. ^{19}F NMR linewidth measurement for this modification suggested a high conductivity due to the fluoride ion.

Many crystalline compounds between antimony trifluoride and alkaline fluoride have been synthesized and characterized by X-ray diffraction[1,2] and ^{123}Sb NQR.[3,4] We have been interested in these halocomplexes because some of these crystals exhibit a characteristic phase transition or a dynamic change in the physical property.[5-8] This is due to the fact that the hypervalent bond has a weak covalent character and shows a characteristic *trans* effect between ligands. In this paper, we report a new fluoride ion conductor $KSbF_4$ and discuss the mechanism of the conduction.

$ASbF_4$ (A : Na, K, Rb, and Cs) were crystallized from dilute hydrofluoric acid containing stoichiometric amounts of Sb_2O_3 and A_2CO_3. The crude crystals were purified by recrystallization from water at room temperature. All samples were identified by powder XRD measurement with a Rigaku Rad-X system using a graphite monochromatized Cu K_α radiation (λ = 1.5405 Å). The electric conductivity was determined by a complex impedance method (ANDO AG-4311B, frequency range from 0.1 to 100 kHz) using a pressed powder pellet coated with carbon electrodes on both sides. DTA was performed using a home-made apparatus with a sealed glass tube. ^{19}F NMR was carried out at 16 MHz with a conventional pulsed spectrometer at the Instrument Center for Chemical Analysis of Hiroshima University.

Figure 1 shows the temperature dependence of the electric conductivity (σ) for $ASbF_4$. All samples showed conductivity lower than 10^{-8} Scm^{-1} at room temperature. However, a steep increase in conductivity was observed for $KSbF_4$ above ca 420 K on heating. The slope changed discontinuously at 455 K, indicating a phase transition to a highly conducting phase with low activation energy. Furthermore, it is interesting that this phase was maintained on cooling, keeping its high conductivity. The conductivity at room temperature is as high as 10^{-4} Scm^{-1} which is slightly smaller than that reported for a fluoride ion conductor $PbSnF_4$ (σ = 10^{-3} Scm^{-1} at 300 K). The activation energies estimated from the $\log(\sigma)$ *vs.* $1/T$ graph were 64 and 27 kJ/mol for the low and high temperature modifications, respectively. In accordance with the conductivity measurement, a strong endothermic peak was observed at 455 K only for the first heating run. These conductivity and DTA measurements on $KSbF_4$ supported that the high-temperature form was metastable and did not return to the original form by repeated thermal cycles. Hereafter we abbreviate the low and high temperature modifications of $KSbF_4$ as α- and β-form, respectively.

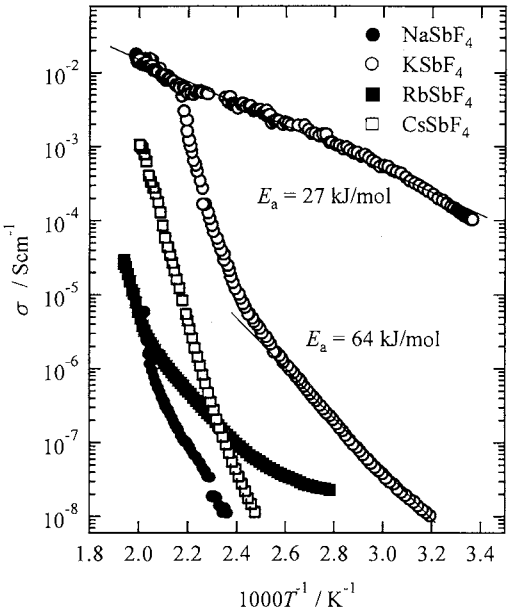

Figure 1. Temperature dependence of the electric conductivity for $ASbF_4$ (A : Na, K, Rb, and Cs).

The XRD patterns of α- and β-form at room temperature are quite different from each other as is shown in Figure 2(a) and (b). The pattern of α-form agreed well with that calculated from its structure, which consists of an isolated tetrameric anion, $(Sb_4F_{16})^{4-}$.[1] The pattern of β-form agreed well with that reported by Davidovich,[3] and it changed to a simple one above 420 K as shown in Figure 2(c). This pattern could be analyzed as a single phase with a cubic lattice (a = 6.059(1) Å, space group = $Fm3m$). Table 1 summarizes crystallographic parameters determined by a Rietveld method.[9] Figure 3 shows the structure of the cubic phase. As is expected from the small unit cell and the space group, the structure could be essentially described as the fluorite structure. In this structure, K and Sb atoms form randomly distributed cationic sub-lattice. Furthermore, the fluoride ions occupy not only original tetrahedral sites but also interstitial octahedral sites. The Fourier synthesis suggested that fluoride ion did not situated at the center of the octahedral site but distributed over the six off-center positions as shown in Figure 3. However, the occupancy factors for F(1) and F(2) are less reliable because of the small scattering factor of a fluoride ion.

Broadline ^{19}F NMR on $KSbF_4$ was observed as a function of temperature in order to confirm the reason for the high conductivity. Figure 4(a) shows the ^{19}F NMR spectra against temperature both on heating and cooling. Figure 4(b) plots the FWHM linewidth against temperature. These graphs show clearly an irreversible phase transition from α- to β-form at T_{tr} in consistent with the conductivity measurement. In the heating process, a motional narrowing begins above ca 250 K and the

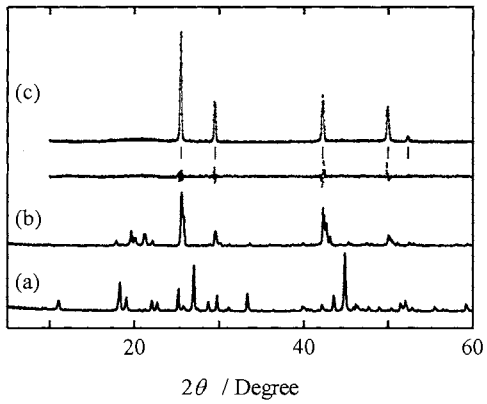

Figure 2. Powder XRD patterns for $KSbF_4$ (a) before and (b) after heating. (c) Final plot of the Rietveld refinement for β-form at 470 K.

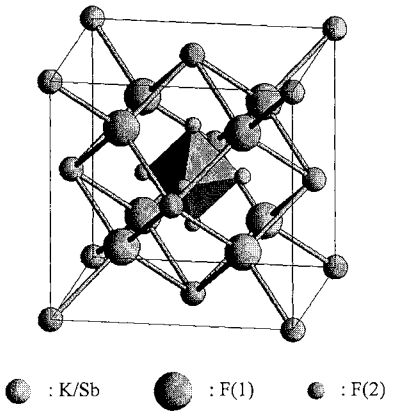

Figure 3. Disordered structure of β-$KSbF_4$ at 470 K.

Table 1. Positional parameters for β-$KSbF_4$[a]

Atom	Position[b]	Ocupancy	x	y	z	B_{iso}/Å^2
K/Sb	a(m3m)	1.0	0	0	0	1.5
F(1)	c(43m)	0.5[c]	0.25	0.25	0.25	5.2(6)
F(2)	e(4mm)	0.167[c]	0.718(4)	0	0	5.0(13)

[a] R_{wp} = 14.7%, R_f = 1.4%. [b] Wyckoff notaion and point symmetry. [c] Tentatively assumed.

linewidth decreases to 3.5 kHz at 440 K. On further heating above T_{tr} it decreases discontinuously to 0.4 kHz which is the narrower limit due to the inhomogeneity of our magnet. This sharp signal suggests the diffusion of the fluoride ion. Furthermore, the sharp signal could be detected down to 250 K on cooling. These NMR measurements proved that the β-form was a fluoride ion conductor and stable over the wide temperature range. In order to estimate the correlation time (τ_c) and the activation energy for the anionic diffusion, the linewidths in the motional narrowing region were analyzed by the following equation,

$$\tau_c = \tan[\pi(\Delta H^2 - A^2)/2(B^2 - A^2)]/\alpha\gamma\Delta H,$$

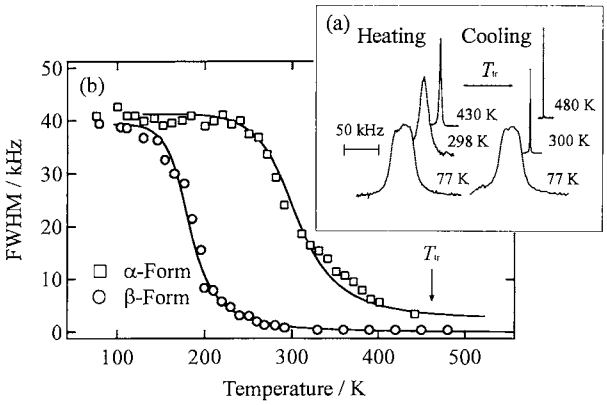

Figure 4. (a) Broadline ^{19}F NMR spectra for $KSbF_4$. (b) FWHM linewidth against temperature for α- and β-form.

and

$$\tau_c = \tau_0 \exp(E_a/RT),$$

where A, ΔH, and B represent the linewidths above, within the transition region, and below, respectively, and α is a constant near unity and γ is the gyromagnetic ratio. A and B were estimated to be 0.4 and 39 kHz from the graph, respectively. The activation energy for the anionic diffusion was determined to be 10.3 kJ/mol for β-$KSbF_4$. This activation energy from the NMR is small compared with the conductivity measurement, suggesting some local motion of the fluoride ion at lower temperature. One of the possible local motions is a translation within an octahedral site.

On the other hand, the electronic conductivity estimated by a four-probe method was $1.4 \cdot 10^{-5}$ Scm^{-1} at 295 K, which was one order smaller than that from the complex impedance method. This difference in conductivity, XRD, and ^{19}F NMR supported an interstitial mechanism for the anion transport in β-$KSbF_4$ similar to anionic conductors with fluorite-type structures.

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