Electrical Conductivity and Fluoride Self-Diffusion in $RbSn_2F_5$

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The electrical conductivity of crystals of $RbSn_2F_5$ has been determined in the range 20–250 °C, and the fluoride self-diffusion by ^{19}F NMR pulsed magnetic field gradients technique for 80–200 °C. Both results show that $RbSn_2F_5$ is a good fluoride conductor even at moderately elevated temperatures. A phase transition is observed near 100 °C.

Studies of the transport properties of SnF_2 and particularly $PbSnF_4$ have shown that these compounds are good ionic conductors [1, 2]. It would be interesting to extend the research for new fluoride super-ion conductors to other compounds based on tin(II) fluoride. The purpose of this work was to characterize the electrical and diffusion properties of $RbSn_2F_5$, first described by Donaldson et al. [3].

Crystals of $RbSn_2F_5$ were obtained from a solution of RbF and SnF_2, molar ratio $RbF/SnF_2 = 1/2$ and well acidified by HF under oxygen free conditions, by means of letting it cool slowly, starting at 90 °C. The crystals precipitated out were filtered, washed with small amounts of cold water and dried in vacuum over KOH. Their geometric shape resembled thin plates.

Mössbauer spectroscopy and X-ray diffraction data for $RbSn_2F_5$ thus obtained agreed well with [3]. The amount of Sn(IV) was less than 1 mol%.

The samples used for conductivity studies were pellets (~ 0.1 cm heigh and $\sim 0.3\ cm^2$ area) obtained by compressing the well ground crystals. Colloidal graphite was used as electrode material. The conductivity measurements were carried out using an A.C. impedance bridge (E8-2) at 20 kHz in vacuum. The frequency dependent dispersion of conductance was found to be negligible above 1 kHz. The measurements were carried out in the temperature range 20 – 250 °C.

The fluoride diffusion was determined between 80 and 200 °C by ^{19}F NMR at 57 MHz and the technique of pulsed magnetic field gradients. Using diffusion times $\Delta = 10 - 20$ ms, the ^{19}F spin echo amplitude A as a function of the amplitude G and the duration δ of the gradient pulses showed unrestricted diffusion at all temperatures studied as the graph of $\ln A$ versus $G^2 \delta^2 (\Delta - \delta/3)$ was linear, and the coefficient of diffusion D_{F^-} was taken from its slope. It varied between $1.5 \cdot 10^{-8}\ cm^2/s$ at 80 °C and $8.5 \cdot 10^{-7}\ cm^2/s$ at 200 °C.

Plots of $\lg D_{F^-}$ and $\lg \sigma T$ versus reciprocal temperature are shown in Figure 1. It can be seen that both curves consist of two parts. The activation energy obtained from the slope of $\lg \sigma T$ versus $1/T$ is 0.47 ± 0.06 eV for the low temperature part and 0.26 ± 0.07 eV for the high temperature part.

The change of the slope of the curves is probably caused by a phase transition of the crystals. A phase transition of $RbSn_2F_5$ at 100 ± 15 °C has also been demonstrated by means of DTA and microcalori-

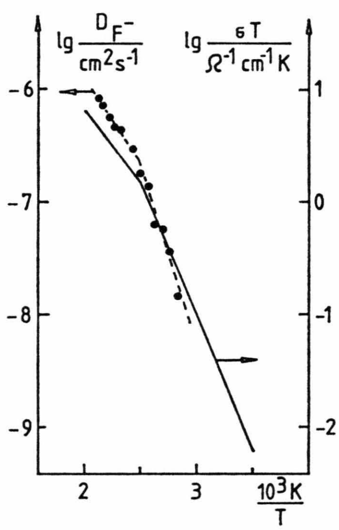

Fig. 1. Arrhenius plot of electrical conductivity and fluoride self-diffusion in crystals of $RbSn_2F_5$. Solid curve: $\lg \sigma T$ at 20 kHz. Points and broken curve: $\lg D_{F^-}$ as determined by ^{19}F NMR PMFG technique.

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metry [4]. The determination of the nature of this phase transition requires further investigations.

It may be noted that the activation energies obtained from the fluoride diffusion and conductivity studies are quite similar at higher temperatures. The electron conductivity measured by means of a Hebb-Wagner polarization method was found to be 10^5 times smaller than the ionic conductivity at 150 °C ($\sigma(F^-$, 150 °C$) \cong 10^{-2}$ ohm cm^{-1}).

These facts prove that $RbSn_2F_5$ is a good fluoride conductor even at moderately elevated temperatures.

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