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POLYMORPHISM OF THE MIXED TIN FLUORIDE Sn_2F_6

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ABSTRACT

The mixed tin fluoride $Sn^{II}Sn^{IV}F_6$ undergoes two phase transitions which have been unambiguously characterized by X-ray diffraction and micro-DTA. They occur at 385 ± 15 K and 470 ± 15 K. Evidence of the $\alpha \rightleftarrows \beta$ transition has also been given from a Mössbauer resonance investigation carried out over the temperature range $77 < T < 450$ K. The γ-high temperature form has been assumed to exhibit the cubic $Fm\bar{3}m$ symmetry ; the structure of the intermediate ß-form is related to the trigonal $LiSbF_6$-type.

MATERIALS INDEX : tin, fluorides

INTRODUCTION

In recent years a lot of compounds with general formula $M^{II}M^{IV}F_6$ have been isolated, in which various structural arrangements have been found depending on the size of the divalent and tetravalent cations (1-3). Some of those investigations have been especially focused on fluorostannates (4,5) : most of the latter compounds crystallize at room temperature either with the rhombohedral $LiSbF_6$-type ($R\bar{3}$ space group) or with the cubic ordered ReO_3-type ($Fm\bar{3}m$ space group).

Some years ago a mixed tin fluoride $Sn^{II}Sn^{IV}F_6$ had been isolated, for which a cubic high temperature form had been characterized (6). The presence of the lone pair on tin difluoride led us to suppose that additional distortions may occur and incited us to investigate further this compound. In particular, Mössbauer resonance spectroscopy seemed to be a suitable technique to observe structural modifications, since the lone pair of Sn(II) strongly affects the s-electron density, giving rise to a relatively large evolution of the Mössbauer parameters ; such a behavior had allowed for instance to distinguish the various forms of SnF_2 (7). Evidence of transitions have also been given by this technique for ternary hexafluorides (8, 9).

This paper is thus devoted to the structural investigation of the mixed tin fluoride Sn_2F_6 using micro-DTA and X-ray diffraction analysis as well as Mössbauer characterization vs temperature.

EXPERIMENTAL

SnF_2 was a commercial product : it was treated under HF stream at 150°C, then heated in vacuum at 100°C and kept in a dry argon atmosphere. SnF_4 was prepared by fluorination of tin difluoride under 2 bar fluorine pressure at 400°C.

Sn_2F_6 was synthesized by solid state reaction of a stoichiometric mixture of the two fluorides. The starting materials were mixed in a dry glove box, introduced into a platinum tube and vacuum heated at 100°C. The tube was then sealed and the reactions carried out at 500°C. The thermal process ended by a temperature quenching.

The sample was characterized by its powder XRD-pattern using Cu Kα radiation. The transition temperatures were determined using micro-DTA : the sample was put into a gold tube sealed in a dry argon atmosphere. The thermal variation of the unit- cell constants was followed using a Guinier-Simon camera.

The Mössbauer resonance spectra were obtained using a constant acceleration Halder-type spectrometer with a room temperature $Ca^{119}SnO_3$ source in a transmission geometry. The powdered samples contained 15 mg natural tin per cm^2, a concentration for which line broadening effect is usually negligible, they were prepared in a glove box. The investigation of the temperature dependence was carried out in a specially built reactor which has been described elsewhere (10). Before recording the spectra the reactor was filled with dry argon. All isomer shifts have been reported with respect to a spectrum of $CaSnO_3$ at 293K.

STRUCTURAL CHARACTERIZATION AND PHASE TRANSITION STUDY

The X-ray diffraction pattern of the sample isolated after quenching does not present any obvious analogy with that of other compounds having the same formulation $M^{II}M^{IV}F_6$. Such a result can probably be related to occurrence of the lone pair which usually leads to distorted environments for tin(II) in fluorides (11-13), leading thus to lower symmetry. Unfortunately attempts to prepare single crystals failed up to now, hindering therefore a precise structural determination of the phase obtained at room temperature.

1) DTA investigation

A micro-DTA study has then been performed between 300 and 600 K, i.e. up to a temperature markedly lower than the melting point previously reported (6). With rising temperature a very weak peak is observed at 385 ± 15 K and a larger one at 470 ± 15K; but the strong slope of the baseline prevents from a more accurate determination of the transition temperatures. As the temperature decreases, only the larger peak is observed. But annealing followed by slow cooling allows to observe again the first weak peak as temperature increases.

2) X-ray diffraction study of the ß- and γ-forms

The transformations have then been investigated using X-ray diffraction from 300 to 520 K. The evolution of the powder pattern is given in Fig. 1. The observed transition temperatures are in good agreement with those characterized by micro-DTA.

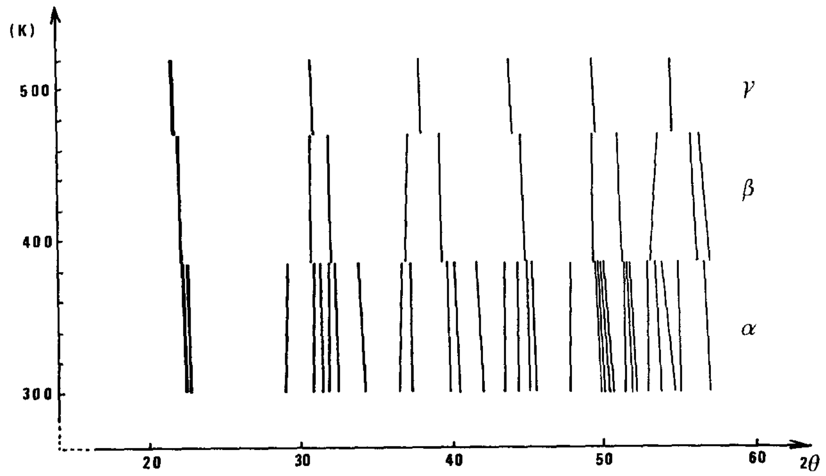

FIG. 1

Thermal dependence of the X-ray diffraction pattern of Sn_2F_6

The high temperature form γ-Sn_2F_6 exhibits a cubic symmetry. All the well observed diffraction lines of the intermediate form ß-Sn_2F_6 can be indexed on the basis of a rhombohedral symmetry ; nevertheless the presence of a few very weak lines cannot be absolutely excluded, although they cannot be accurately measured. On the other hand, no additional lines characterizing a superstructure are detected on the diffraction pattern, which could let suppose that the ß- and γ-forms crystallize respectively with VF_3- and ReO_3-type. Such a behavior results probably from the very weak difference between the diffusion factors of divalent and tetravalent tin. A similar feature had already been previously reported in the mixed thallium fluoride Tl_2F_3 (14). These results can in particular be compared to that found for Pd_2F_6, in which cationic ordering was unambiguously shown by neutron diffraction (15).

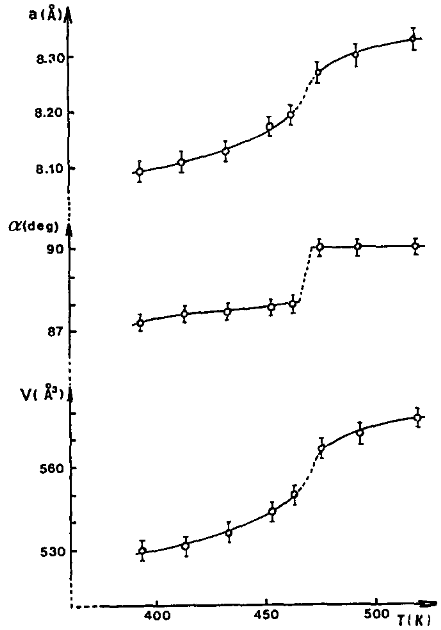

FIG. 2

Thermal variation of the unit-cell parameters and volume of β- and γ-Sn_2F_6

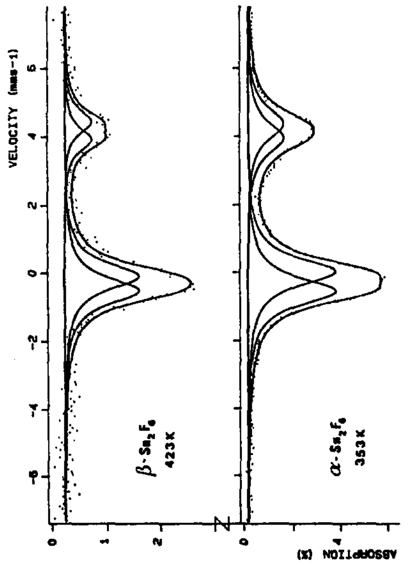

FIG. 3

Mössbauer resonance spectra of α-Sn_2F_6 and β-Sn_2F_6

The relatively wide size difference between tin (II) and (IV), as well as the presence of a lone pair for tin(II) allowed us to predict also a cationic ordering in Sn_2F_6 : in the scope of such an assumption the β- and γ-forms would be of rhombohedral $LiSbF_6$-type and of cubic ordered ReO_3-type respectively. The thermal variation of the unit cell constants and volume from 393 to 520 K is given in Fig. 2. For β-Sn_2F_6 the unit-cell taken into account was the rhombohedral pseudo-cubic cell with an α-angle close to 90° (16). The parameters deduced on both sides of the $\beta \xrightleftharpoons{470\pm15K} \gamma$ transition temperature are then the following:

453K a=8.17±0.01 Å; α = 87.8±0.2°

477K a = 8.27±0.01 Å

^{199}Sn MÖSSBAUER STUDY

The Mössbauer resonance investigation has been carried out between 77 and 450 K. Above this temperature the compound reacts partially with the metallic sheets of the aluminium sample holder, giving thus rise to a gradual reduction of tin (IV) and yielding the formation of Sn_3F_8 ; the use of gold sheets has allowed to avoid such a reaction, but the whole γ radiations are then practically absorbed and no spectrum could be observed.

Only domains corresponding to α- and β-Sn_2F_6 can therefore be investigated. The Sn Mössbauer spectra of both allotropic forms are given in Fig. 3, at 353 and 423 K respectively. It should be noted that the resolution obtained for the β-phase is less accurate than that of the α-phase due to short counting times required for hindering formation of Sn_3F_8.

A previous Mössbauer resonance investigation of α-Sn_2F_6 at low temperature had shown a relatively high value of the quadrupole splitting for Sn(IV) and a weaker one for Sn(II): such results had been attributed to an asymmetry of the electronic charge distribution around the Sn nuclei (10).

If we assume that the symmetry of the tin (II) and tin (IV) environments is disturbed during the conversion from α into β, a modification might result in the evolution of the quadrupole splitting. This assumption is verified as shown on the temperature dependence of the quadrupole splitting of Sn(II) and Sn(IV) (Fig. 4): a strong discontinuity takes place at transition temperature. As temperature increases, the environment of tin(IV) and tin(II) in α-Sn_2F_6 can be considered as becoming more symmetrical since the value of Δ gradually decreases. When the transition occurs, the quadrupole splitting is modified in opposite directions for the two nuclei: such an increase in the case of Sn(II) seems a priori surprising because it could reveal a larger asymmetry of tin(II) surrounding or a higher covalency in the β- form. But a similar feature has already been previously reported for the $\alpha \rightleftarrows \beta$-$SnF_2$ transition : it has been attributed to a different stereochemistry of the lone pair in both phases (7). Above transition temperature the value of Δ appears constant for the two nuclei, but the investigated temperature domain is too narrow to ascertain such a behavior. It is likely that at higher temperature the symmetry of the two sites would increase again similarly.

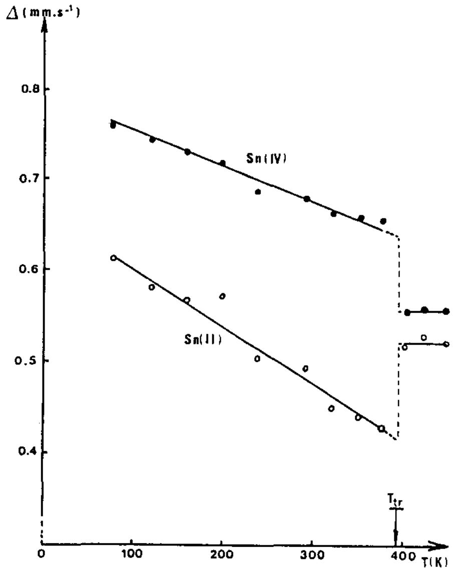

FIG. 4
Temperature dependence of the quadrupole splitting of Sn(II) and Sn(IV) in Sn_2F_6

CONCLUSION

The existence of three allotropic forms for Sn_2F_6 has been characterized by micro-DTA and X-ray diffraction. The $\alpha \rightleftarrows \beta$ transition, which had not been detected earlier, had in addition been confirmed by Mössbauer spectroscopy from the temperature dependence of the quadrupole splitting. Although the powder pattern of the two high temperature forms , as it could be expected, do not show the occurrence of a superstructure, they may be assumed to be related to the $LiSbF_6$-type and the ordered ReO_3-type structure respectively. A crystal diffraction study will be carried out to determine unambiguously the cationic ordering and surrounding. Attempts to prepare single crystals are now in progress.

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