

THERMOCHEMISTRY OF VITREOUS ANTIMONY ORTHOPHOSPHATE

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A vitreous form of antimony orthophosphate has been obtained using antimony polyphosphate as a precursor. Morphologically, it is composed of small uniform grains having ellipsoidal shapes. Prolonged thermal treatment leads to the transformation into a crystalline variety. According to TG curves, both forms start to evaporate at 920°C without decomposition. Melting point of crystalline SbPO₄ has been determined to be 877°C. Thermomechanical study reveals plastic behavior due to the capacity to flow under shearing stress. Ceramics formation in the system Sb₂O₃–SbPO₄ is discussed. The presence of glass domains in this system has not been confirmed.

Keywords: antimony orthophosphate, glasses, inorganic materials

Introduction

Crystalline antimony orthophosphate is a well known compound which is used for the synthesis of Sb(III) layered materials and glasses [1]. It belongs in a monoclinic system [2] and exhibits very particular structural features due to unpaired electronic pair at the Sb atom, according to [3]. One of the structural consequences of its presence is the unilateral close coordination of 3–5 ligands near the Sb atom. The aforementioned electronic pairs do not allow other ligands to come closer to Sb(III) and at least two options for structure formation are possible: 1) when Sb(III) polyhedra are connected through asymmetric bridging ligands and 2) when they are oriented by opposed electronic pairs. The latter are located at one of the apices of a trigonal bipyramid forming infinite layers {Sb(PO₄)}_{2∞} bonded through Van der Waals interactions [4].

These considerations are applied to the crystalline form, but it can be easily supposed that, owing to geometric impediments, the formation of {Sb(PO₄)}_{2∞} layers may be altered and delayed. On the other hand, the interaction of covalent bonds with unpaired electrons frequently leads to the formation of three-centered bonds, and as a result, to the polymerization processes [5]. As all the prerequisites for glass formation are fulfilled, the existence of SbPO₄ vitreous form can be stipulated. Such a form, however, has not yet been isolated in spite of its demand and chemical suitability for the preparation of stable antimony-containing glasses. As the vitreous form would not bear any SbPO₄ crystals capable of acting as a devitrification activator [6], it might serve as a convenient inert batch component. Nevertheless, the

conventional synthetic techniques involving ionic interactions in solutions [7, 8] cannot be used because of swift nucleation and subsequent crystal growth of monoclinic SbPO₄. On the other hand, the processes of SbPO₄ vitreous variety formation appear quite promising when the starting material is a viscous melt and the elimination of a volatile component can be controlled. Consequently, one of the most convenient ways of preparation may be the decomposition of polymeric phosphate Sb(PO₃)₃ [9]. The aim of the present work is to study the mechanisms of formation and some physico-chemical properties of vitreous SbPO₄. As shown in recent publications, it may be successfully done using thermal analysis in association with other instrumental techniques [10].

Experimental

Starting reagents were phosphoric acid H₃PO₄ and antimony(III) oxide, both of analytical grade purity from Merck. Sb(PO₃)₃ was specially prepared according to [11]. Crystalline antimony orthophosphate was prepared according to [8] with some modifications. This compound was identified by chemical analysis and X-ray powder diffractogram as a high purity single phase (ICSD file 35-0829). Thermal behavior was studied by thermal gravimetric analysis (TG), differential thermal analysis (DTA) and thermomechanical analysis (TMA), both apparatuses being from 50H Shimadzu Instrumentation. Measurements were carried out using synthetic air; heating rate 10–15°C min⁻¹. Chemical analysis for Sb and P was carried out by ICP technique with multi-element stan-

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standard solution IV, Merck AG. Scanning electron microscopy (SEM) was carried out using a SM-300-TOPCON instrument. X-ray diffraction patterns were registered with a Siemens Kristalloflex diffractometer with a graphite diffracted beam monochromator and Ni filter, 2θ range $4\text{--}70^\circ$.

Results and discussion

Previously registered TG curves of polyphosphate $\text{Sb}(\text{PO}_3)_3$ showed that after 500°C the compound becomes a viscous mass and at 800°C starts to lose mass, according to the reaction:



This process is extremely slow and cannot be brought to an end during conventional TG procedure, since the time of heating at a plateau should be much longer than this equipment can permit. Unquestionably, this is due to the gradual disintegration of $\text{Sb}(\text{PO}_3)_3$ polymeric chains in a milieu with high viscosity where diffusion is poor. The polyphosphate samples were heated at 800°C for 18, 70 and 120 h and mass losses recorded. In fact, after 18 h, mass stabilization was achieved and chemical analysis rendered the following results (mass%): Found: P – 15.28; Sb – 55.86. Calculated for SbPO_4 : P – 14.30; Sb – 56.17.

X-ray powder patterns presented in Fig. 1 show that the sample heated at 1100°C for 120 h is a crystalline SbPO_4 , in accordance with the ICSD powder file 35-0829, while the samples treated at 800°C even for longer periods are amorphous (vitreous) compounds. This means that the vitreous form is stable at least until 800°C and temperature (and consequently diffusion) appears to be a major factor. It does not mean, however, that mass loss had achieved a plateau, as follows from prolonged mass measurements. As a series of X-ray diffraction patterns reveals only a single orthophosphate phase and no traces of antimony oxide, this fact suggests the volatilization of SbPO_4 , which was confirmed by

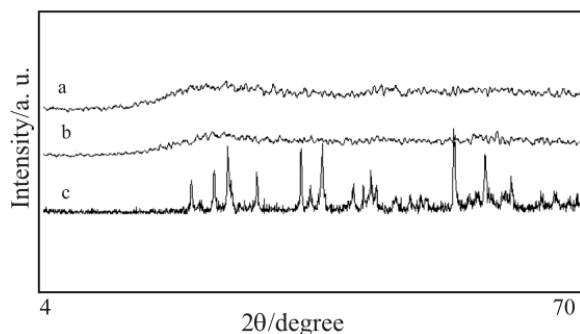


Fig. 1 X-ray patterns of the $\text{Sb}(\text{PO}_3)_3$ decomposition products. a – after heating at 800°C for 18 h; b – after heating at 800°C for 120 h and c – after heating at 1100°C for 70 h

comparison with the mass loss of pure crystalline SbPO_4 at the same temperatures. Besides, the thermogravimetric curve of the latter compound exhibits a sharp mass loss onset at ca. 920°C .

DTA curves of pure crystalline SbPO_4 and crystallized vitreous form are represented in Fig. 2. The heating curves show that melting of SbPO_4 would occur at approximately 850°C , although the corresponding exothermic effects are rather diffuse. On the other hand, crystallization peaks on the cooling curves are well pronounced giving a melting point temperature of 877°C . No perceptible glass transition points were detected. It seems that the change from the highly viscous state to a liquid state (and vice versa) is not accompanied by a considerable thermal effect.

In Fig. 3 the TMA curves of the vitreous form are compared with the curves of the crystalline orthophosphate. Both samples were tested twice, augmenting the load during the second experiment. In the case of a crystalline solid submitted to the relatively low load, a classic dilatation pattern would be expected.

Meanwhile, the curve corresponding to the sample heated for 18 h is decrescent during heating, and almost parallel to the temperature axis during cooling. This behavior was reproduced repeating the experiment with a much heavier load (10 g), although the slant seems to be less pronounced. For a polycrystalline body it could be interpreted as contraction of a compound having negative dilatation coefficient. As this is not the case, the sample being amorphous, the deformations which have been produced under stress do not disappear and we see a plastic response of the material in question.

The fact that even after the first cycle of treatment the curve shows a certain incline, may be explained taking into account the capacity to flow under shearing stress which had not been depleted during the previous operation. As a rule, this residual capacity to flow is extremely difficult to detect and only a significant increase in the load mass allows it to be

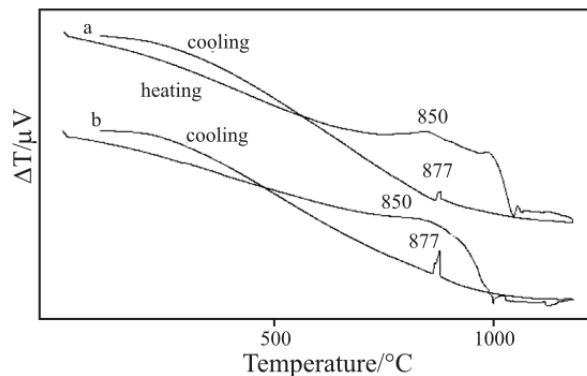


Fig. 2 Comparison of DTA curves (heating and cooling) of SbPO_4 obtained by different ways: a – crystalline SbPO_4 ; b – SbPO_4 obtained after crystallization of vitreous form

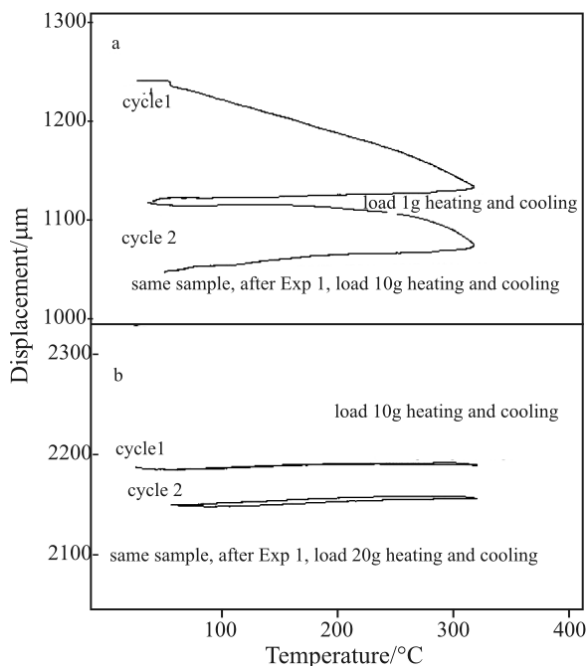


Fig. 3 TMA curves of the samples heated for a – 18 h and b – 120 h, corresponding with the vitreous and crystalline forms of SbPO_4

detected. The deformation occurs as a result of large anionic layers shifting along the plane of contact, this process not being accompanied by rupture of intermolecular bonds. Such a phenomenon is well known in the field of polymers [12] and logically has relevance for antimony orthophosphate because of its arrangement in the form of similar infinite chains $\{\text{Sb}(\text{PO}_4)\}_{2\infty}$ represented in Fig. 4.

In the glass these chains are distorted and their alignment is what ultimately provides for the devitrification process. As expected, the sample treated for 120 h had lost its plasticity, but its structure remained still imperfect, so it is natural that under the load of 10 g both heating and cooling curves are superposed. Moreover, the second experiment with the same sample still exhibits a slight dilatation even under the load of 20 g.

Electronic microscopy allows us to see clear morphological parallels to the above discussed plastic behavior. As a rule, at high augmentations, the surface of

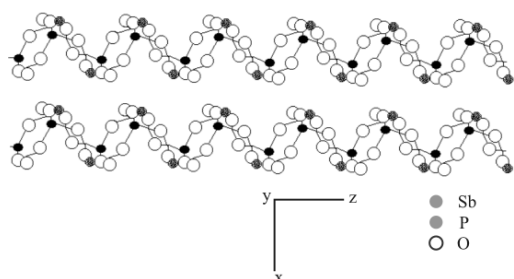


Fig. 4 Infinite chains in SbPO_4 built up according to structural data from [4]

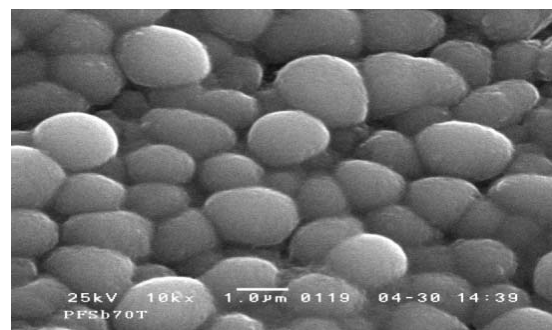


Fig. 5 SEM image of the SbPO_4 vitreous form

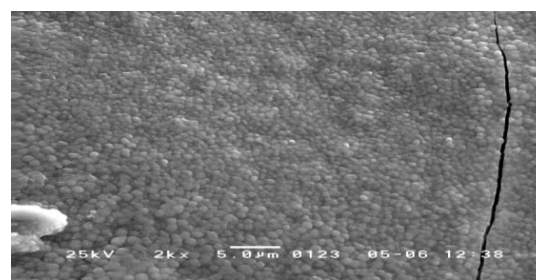


Fig. 6 SEM image of the fissure showing elastic deformation

vitreous antimony orthophosphate is composed of small uniform grains having ellipsoidal shapes (Fig. 5). The SEM image represented in Fig. 6 shows an edge of the sample treated for 18 h, where one can see how the cutting action had produced sliced slivers and small chips spread along the lateral surface.

These patterns are characteristic for TMA measurements of polymethylmetacrylate, polyethylene and other polymeric materials, showing mass flow instead of sharp rupture created as a result of elastic deformation [13]. Yet the compound treated mechanically at room temperature clearly shows a narrow opening crack of considerable length and depth characteristic of fragile materials with elastic properties.

In this context one of the most interesting problems is the possibility of glass formation in the system $\text{Sb}_2\text{O}_3\text{-SbPO}_4$. It was reported elsewhere [14] that this had been observed in a wide range of concentrations, at least from 10 to 70 mol% Sb_2O_3 . It seems very strange from the theoretical point of view, as the shortage of glass forming PO_4 tetraedra should have increased the tendency to form crystalline phases and not otherwise. In fact, a recently obtained antimony(III) phosphate $\text{Sb}_5\text{PO}_{10}$ (or $\text{Sb}_2\text{O}_3\cdot\text{SbPO}_4$), is not a vitreous but a crystalline compound, whose structure has been recently resolved [15]. It belongs in a monoclinic system and is composed of alternating layers of antimony oxide and antimony orthophosphate. The antimony oxide layer is a double sheet, which ‘dilutes’ a relatively small number of chains, so glass formation with this – and even lower – content of Sb_2O_3 is extremely improbable.

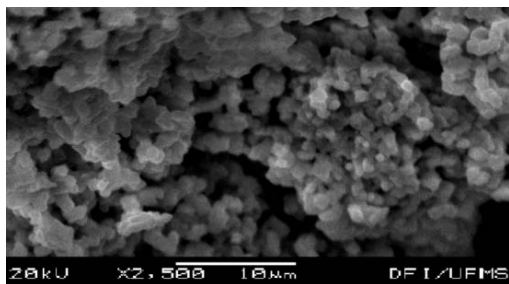


Fig. 7 SEM image of a typical ceramic in the system $\text{Sb}_2\text{O}_3\text{-SbPO}_4$

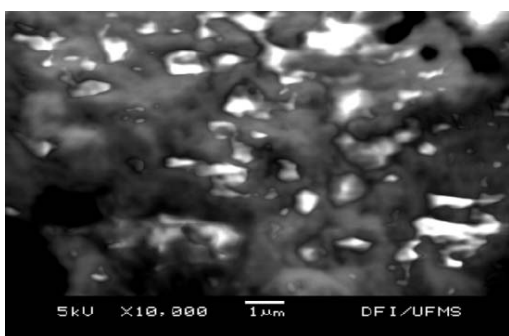


Fig. 8 Melting of ceramic under electron beam

We actually carried out the study of the system $\text{Sb}_2\text{O}_3\text{-SbPO}_4$ working precisely under the reported conditions [14] but have been unable to reproduce the data described in that work. All samples obtained under heating were typical ceramics with pronounced crystallite agglomerates in the areas of intensive growth, as is shown by a characteristic SEM image in Fig. 7. The X-ray phase analysis of the sample 2:1 allowed the identification of the crystals. As expected, it is the aforementioned oxophosphate $\text{Sb}_5\text{PO}_{10}$ described in [15] despite of totally different way of formation. In the samples with higher phosphorus content SbPO_4 , being amorphous, was not detected in the diffractograms.

These ceramics are extremely sensitive to an electronic beam: after 5–10 s of exposure they melt, losing outline and distinctness (Fig. 8), and therefore might have been easily mistaken for glasses by the author of [14].

Other possible source of error may be the usage of some other compound instead of antimony orthophosphate which, according to the original text, has not been previously identified either by chemical analysis, or by X-ray diffraction.

The detailed study of the system $\text{Sb}_2\text{O}_3\text{-SbPO}_4$ and its applications is in progress.

Conclusions

A vitreous form of antimony orthophosphate can be obtained by the decomposition of polyphosphate.

Morphologically the compound is composed of small uniform grains having ellipsoidal shapes. Above 920°C both vitreous and crystalline forms start to evaporate without breaking up. Under mechanical deformation the vitreous form shows typically plastic behavior. The presence of glass domains in the system $\text{Sb}_2\text{O}_3\text{-SbPO}_4$ has not been confirmed.

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