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DECOMPOSITION OF FERROELECTRIC $LiH_3(SeO_3)_2$

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Previously reported surface transformation of ferroelectric $LiH_3(SeO_3)_2$ from crystalline to amorphous state at $T_a = 80°C$ is studied by means of the thermal analysis (DTA, TGA) and the observation of X-ray diffraction patterns. We find an endothermic reaction (DTA) as well as a reduction of the sample weight (TGA) starts at about T_a with increasing temperature. In accordance with this, X-ray halo intensity gradually develops above about T_a at the expense of Bragg diffraction intensity. It is concluded that the surface transformation originates from the decomposition having a long characteristic time.

1. INTRODUCTION

IT IS KNOWN that ferroelectric $LiH_3(SeO_3)_2$ (abbreviated LTS) exhibits no ferroelectric phase transition under atmospheric pressure because of an occurrence of melting at $T_m = 110°C$ [1]. The latent ferroelectric phase transition is estimated to be $T_t = 147°C$ from the extrapolation of a high-pressure experiment [2]. The crystal structure was determined at room temperature [3, 4]. The space group is *Pn* and the monoclinic unique axis is parallel to the *b* axis. This compound displays a large electric conductivity of about $10^{-2}\,\Omega^{-1}\,m^{-1}$ above 80°C or more [5]. The direction of spontaneous polarization varies with temperature in the plane perpendicular to the *b* axis. A large spontaneous polarization, $15\,\mu C\,cm^{-2}$ at room temperature, is observed along the *c* axis [1].

Recently an unexpected reduction of X-ray diffraction intensity has been reported above about $T_a = 80°C$, though no practical change of the crystal structure takes place at T_a [6]. It has been concluded that the reduction of the intensity comes from a transformation from crystalline to amorphous state of the surface area of LTS. It is, however, uncertain what the origin of the curious phenomenon is. The aim of the study is to clarify the origin of this phenomenon.

2. EXPERIMENTAL

Colorless single crystals were grown by cooling at a rate of $0.1°C\,day^{-1}$ an aqueous solution of Li_2CO_3 and H_2SeO_3 in the stoichiometric molar ratio 1 : 4 after two times recrystallizations. In the early study, the differential thermal analysis (DTA) was made with using a hand-made setup detecting no anomaly at T_a [6]. Here, we carried out again the DTA measurement with higher accuracy along with the thermal gravitational analysis (TGA) using an apparatus TGD-5000RH. Powdered crystal sample of which weight is about 60 mg was used for every measurement. As the standard sample, same amount of α-alumina (Al_2O_3) was used. All measurements were carried out by heating run. The speed of heating was chosen in the range from 0.5 to $4.0°C\,min^{-1}$ and kept constant in the respective runs.

To complement the thermal analysis, X-ray scattering patterns from crystal plates was observed with varying temperature. Patterns were measured in the θ–2θ scanning mode using a Rigaku RAD-A two-circle diffractometer with Cu–$K\alpha$ radiation.

3. RESULTS AND DISCUSSION

Figure 1 is the experimental result of DTA and TGA of the powdered sample in the heating run. We detect clearly an endothermic reaction in the curve of DTA as well as a reduction of the sample weight in the curve of TGA. It is to be noted that the endothermic reaction and the reduction of the sample weight start at about 80°C which coincides with the reported surface transformation temperature T_a [6]. The results show that the decomposition begins at about $T_a = 80°C$. In addition to this anomaly, a great endothermic reaction is observed in the DTA signal at $T_m = 110°C$. This is due to the known anomaly of the melting of the crystal bulk. Two kinds of anomalies at T_a and T_m are reproducible in the heating run.

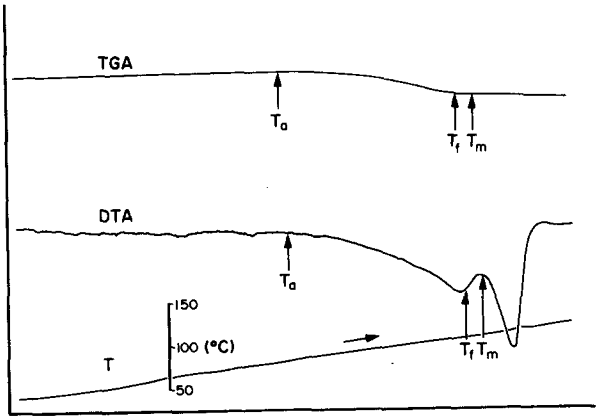

Fig. 1. Temperature dependence of DTA and TGA. The straight line T denotes the temperature (°C). The measurement is the heating run ($1.0°C\,min^{-1}$). $T_a = 80°C$ is the decomposition temperature and $T_m = 110°C$ the melting temperature. T_f denotes the third anomaly (see text). Note that the record of DTA is advanced while that of TGA is retarded with respect to the record of T.

It should be noticed that third anomaly is observed at the temperature by several degrees lower than T_m. Around this temperature, called T_f hereafter, the reduction of the sample weight (TGA) becomes unappreciable in the heating run. Near T_f of about 105 K, the DTA signal turns upward indicating suppression of the endothermic reaction which starts at T_a. We think that this phenomenon is associated with the fact that the sample surface becomes viscous fluid above about T_f. It was, indeed, observed that the powders in the sample coalesce with each other below the melting temperature T_m, then the effective surface area of the powdered samples becomes very small above T_f. This will cause to slow down the decomposition rate. Therefore, we can understand this anomaly is a secondary effect at the surface area accompanied by the decomposition rather than the premelting phenomenon of LTS.

To verify the decomposition from another aspect, we carried out the thermal analysis for the powdered sample which had been exposed in the air of the temperature in the range $T_a < T < T_m$ for a long time, a week or more. We crushed the samples frequently in this interval to promote the transformation. We found no anomaly at both 80°C (T_a) and 110°C (T_m) in these samples to indicate again this transformation is the decomposition. We confirmed that the decomposition has basically no relationship to H_2O, O_2 and other active components in air because quite a similar result as given in Fig. 1 is obtained for the measurement in which the sample cell is filled with a N_2 gas. It is natural to suppose, therefore, that the decomposition of LTS is completed under the condition that surfaces are in contact with free space.

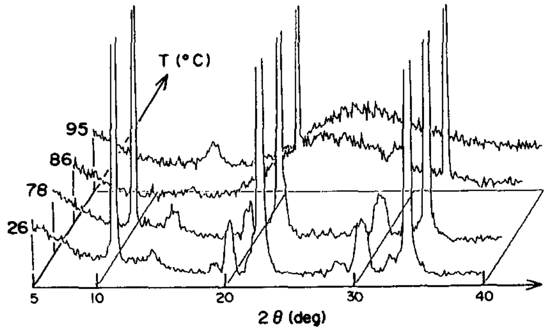

Fig. 2. Temperature variation of the X-ray scattering intensity from a plate which is a single crystal at room temperature (heating rate $\sim 1°C\,min^{-1}$, Cu$K\alpha$, θ–2θ scan). The change of halo patterns means the decomposition develops with increasing temperature.

Here, we notice that crystals become fluid with high viscosity with a brownish red color in the high temperature region. This strongly suggests that Se and H_2O are isolated from the crystals by the decomposition. In addition, we often observed transparent whisker-like crystals on the walls around the sample cell after thermal measurements have ended. It seems that the decomposition of LTS has a rather complex process and we leave aside what materials are produced by the decomposition. At any rate, it is very likely that the high electrical conductivity above T_a [5] comes from the dissociated ions or ionic groups.

We mounted a single crystal plate on an X-ray goniometer at room temperature. Figure 2 demonstrates temperature variation of the X-ray scattering patterns from this plate. We see that halo patterns grow considerably above T_a while Bragg intensity reduces with increasing temperature. This indicates that the decomposition achieves with increasing temperature.

In conclusion, we should like to mention how the decomposition has influences on measurements. We notice that previous measurements of LTS and the deuterated analog have been restricted in the temperature range below about 90°C [1, 5, 7–10]. We suppose that this limitation comes from circumstances that the characteristic time of the decomposition becomes smaller than the time required for measurements with increasing temperature. Probably, it is valid to make measurement under the condition that the sample is shielded from free space to lower the decomposition rate.

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