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Low Frequency Dispersion and Quasi Two-dimensional Proton Conductivity in $(NH_4)_3H(SeO_4)_2$

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Abstract

A dielectric measurement ranging from 1 kHz to 1 MHz revealed the low frequency relaxational dispersion in phases I, II and III of $(NH_4)_3H(SeO_4)_2$. Its anisotropic AC electric conductivity for high frequency limit was quasi two-dimensional. These facts can be explained through the proton transfer in a unique arrangement of proton which resides in a dimer of SeO_4-H-SeO_4. The application of strong electric field gave rise to a double or more complicated dispersion.

Key words: triammonium hydrogen diselenate, superionic conduction,
dielectric dispersion, ferroelectrics, phase transition

$(NH_4)_3H(SeO_4)_2$ is known to exhibit a successive phase transition with six phases[1-3] denoted as from I to VI with decreasing temperature. The phases I and II are superionic phases[4-6] which can be explained by the unique arrangement of proton network. In general, this crystal is fairly rich in proton and proton conductive by nature. There are one acid proton and twelve ammonium protons in a unit formula. The acid proton, much fewer in number though, plays an important role for higher conduction in the superionic phase. It functions as a loose binder for a dimer of SeO_4-H-SeO_4 bound by means of hydrogen bond in a double minimum potential, it also forms a layer structure parallel to (100) plane and resides so as to satisfy the crystal symmetry in phase III[7] (triclinic $C\bar{1}$). However in the trigonal phase (I and II) the proton and its parent SeO_4 pyramidal tetrahedron take a dynamically fluctuating structure, therefore the possible number of position of acid proton is tripled with lower chemical potential. Consequently the acid proton can more easily transfer within the layer than between layers, which explains an extaordinary high AC electric planar conductivity in phases I and II. The acid proton arrangement within a layer projected on (100) for both

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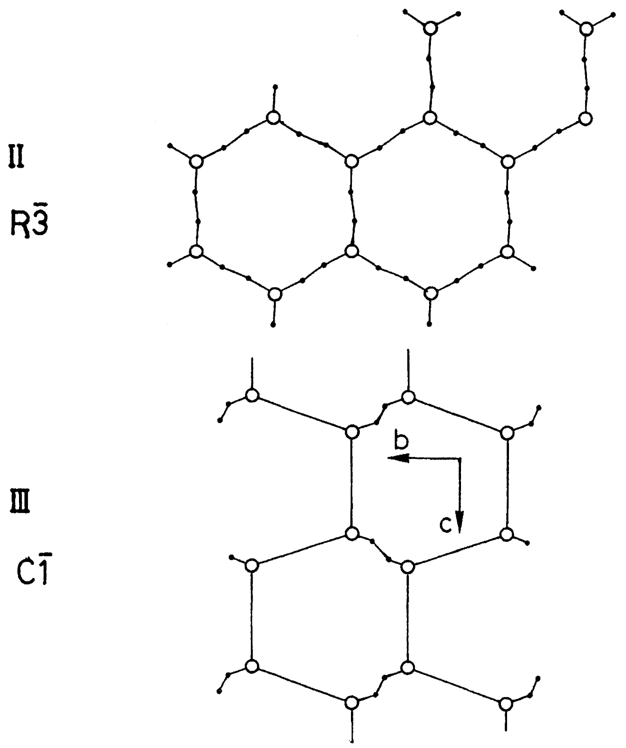

Fig. 1. Sketch of proton arrangement within a layer projected on (100) in phases II and III.

monoclinic and trigonal phases is depicted in Fig. 1 where the possible proton position is black point and the vertex oxygen of SeO_4 is open circle.

In order to confirm the aforementioned picture of proton conduction, we carried out a dielectric measurement within the phases I, II and III using HIOKI LCR HI TESTER 3530 with the frequency range from 1 kHz to 1 MHz.

Single crystals were grown from a stoichiometric aqueous solution of $(NH_4)_3H(SeO_4)_2$ and H_2SeO_4 by slow evapolation in a refrigerator. The axis system is determined as A. Pietraszko[7] adopted which is different from that of Gesi's system[1]. The samples were cut and shaped with an approximate dimension of 4×5×1 mm and painted with a silver paste as electrodes.

In Fig. 2 the typical complex conductivity along *c* axis in superionic phases with an electric field intensity of 1.5V/cm is presented. As a Cole-Cole plot of complex dielectric constant in a relaxational type of dielectrics tells us, this semi-circle manifests the existence of low frequency dielectric dispersion of relaxational type. This dispersion frequency range is consistent with the correlation time derived from ESR[8] of VO^{2+} through a motional narrowing.

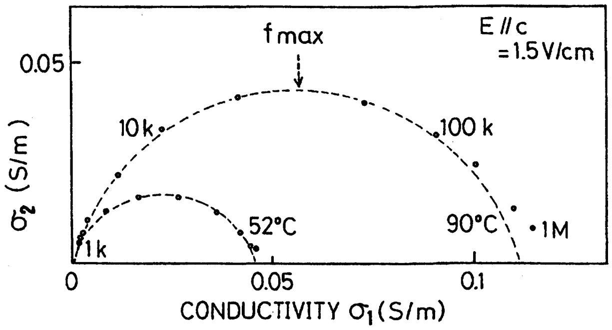

Fig. 2. Diagram of complex conductivity along *c* at 52 and 90°C.

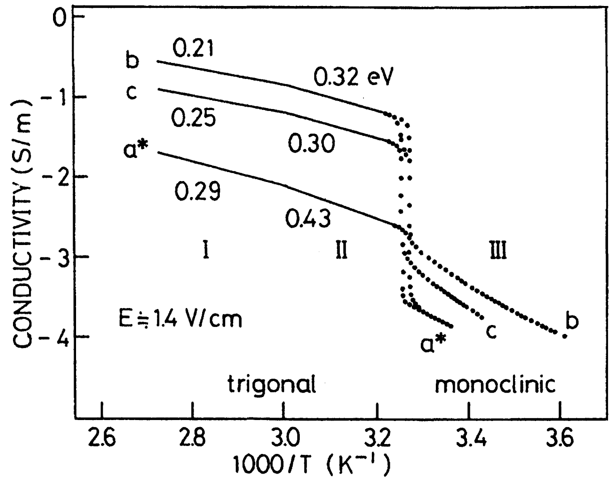

Fig. 3. Temperature dependence of AC electric conductivity at high frequency limit.

In Fig. 3 the temperature dependence of real conductivity at high frequency limit is summarized together with the activation energies drawn along each line respectively. It is obvious that planar (*b* and *c*) conduction is much higher than inter-layer conduction namely along *a**. Although taking the experimental error into account it is delicate to draw a conclusion, the result shows that the conductivity at high frequency limit along *b* axis is higher than that of *c* by the factor of about 2.

We also found an electric field intensity dependece of conductivity dispersion. In Fig. 4 an example is shown at 90°C along *b* axis at 1.4, 14 and 28 V/cm. At 14 V/cm a double arc appeared which, we estimate, corresponds to far and near hopping mechanism of proton. The result implies that in a strong field the proton can transfer beyond the nearest bond but less frequently. Though we found an interesting new fact, as both frequency and electric

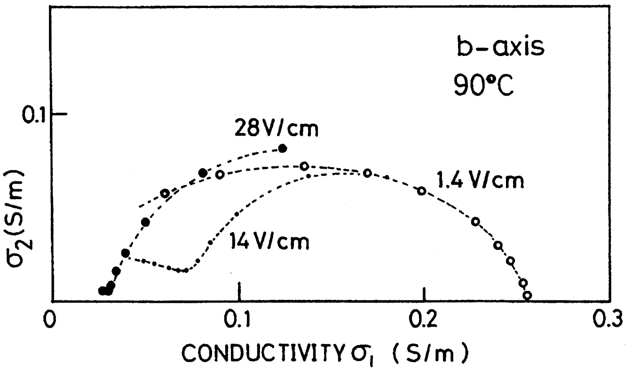

Fig. 4. Electric field intensity effect on conduction dispersion.

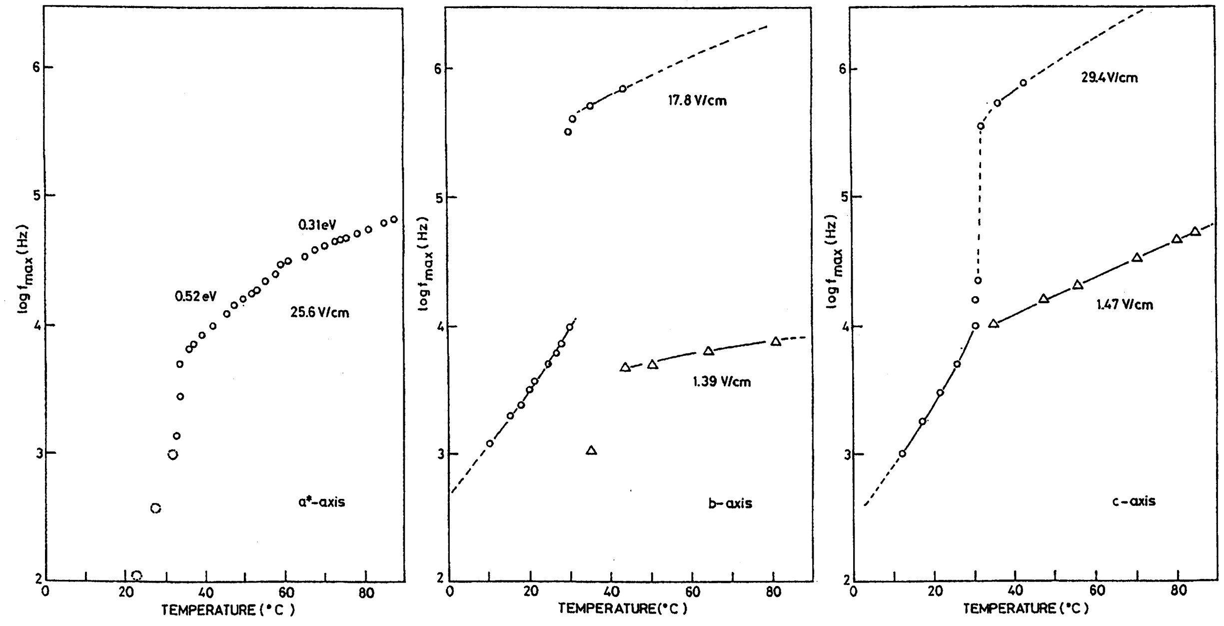

Fig. 5. Temperature dependence of f_{max}.

field intensity range are not yet satisfactory, wider range and more comprehensive measurement is necessary to gain an insight in the nature of proton conduction of this crystal.

Next we pay attention to the relaxation time. As a measure of relaxation time we plotted the frequency f_{max} where the imaginary part of the conductivity have the maximum value with regard to a major semi-circle. In Fig. 5 f_{max} is plotted as a function of temperature for each axis. Compared to *b* and *c*, the f_{max} along *a** is obviously low in a strong electric field and that we could not determine the f_{max} in a weak field because it is too low beyond the experimental range.

In conclusion we have succeeded to show the quasi two-dimensional proton conductivity and its dynamical feature with the electric field intensity effect. However there still exist some problems such as a quality of sample including non-stoichiometry and a thermal history, an electric field history, a chemical reaction at the electrodes, a surface conduction and so forth. As these matters sensitively affect the result, we must forward the experiment more meticulously to get rid of every possible apprehensions.

References

1) K. Gesi: J. Phys. Soc. Jpn. **42** (1977) 1785.
2) T. Osaka, Y. Makita and K. Gesi: J. Phys. Soc. Jpn. **46** (1979) 577. and references therein.
3) M.A. Augustyniak, S.K. Hoffmann, J. Goslar, W. Hilczer and J. Wolak: Ferroelectrics Letters, **15** (1993) 69.
4) K. Furukawa, S. Akahoshi, T. Fukami and K. Hukuda: J. Phys. Soc. Jpn. **59** (1990) 4560.
5) K. Furukawa: Rep. Fac. Sci. Kagoshima Univ. **24** (1991) 47.
6) K. Furukawa: Rep. Fac. Sci. Kagoshima Univ. **25** (1992) 47.
7) A. Pietraszko, K. Lukaszewicz and M.A. Augustyniak: Acta Crystallogr. **C48** (1992), 2069.
8) K. Furukawa: Read at the 49th Annual meeting of the Phys. Soc. Jpn., Fukuoka, March, 1994, 29a-YR-12 (Advance abstracts Vol. 2, p. 87)