

Calorimetric and Raman Spectroscopic Studies on the Low Temperature Phases of Trirubidium Hydrogen Diselenate and Its Deuterated Analogue

Mie Mie Thin

Abstract

The average specific heat capacities ($\overline{C_p}$) of Trirubidium Hydrogen Diselenate $Rb_3H(SeO_4)_2$ and its deuterated analogue $Rb_3D(SeO_4)_2$ were measured in the temperature range from 77K to 300K. The $\overline{C_p}$ of $Rb_3D(SeO_4)_2$ is slightly larger than that of $Rb_3H(SeO_4)_2$. There may be thermal anomaly in $Rb_3D(SeO_4)_2$ at the low temperature. A Raman Scattering line observed in the paraelectric phase splits into two lines at 90K. Thus, the antiferroelectric-paraelectric phase transition of $Rb_3D(SeO_4)_2$ occurred in the temperature below 90K.

Key words: Specific Heat Capacity, Raman Scattering, $Rb_3H(SeO_4)_2$, $Rb_3D(SeO_4)_2$.

Introduction

Trirubidium Hydrogen Diselenate, $M_3Rb_3H(SeO_4)_2$ (abbreviated as TRHSe) is a member of $M_3H(XO_4)_2$ - type hydrogen-bonded crystals, where $M = K, NH_4, Rb, Cs$ and $X = S, Se$. All the compounds in the family crystallize in the monoclinic space group $A2/a$ ($Z = 4$) at room temperature with the exception of $Cs_3H(SeO_4)_2$, which adopts a different but very similar structure belonging to the space group $C2/m$ ($Z = 2$). Some of the crystals in this group exhibit a phase transition below room temperature. The transition temperatures are strongly affected by deuteration and the isotope effect is remarkably large for $K_3H(SO_4)_2$, $Rb_3H(SO_4)_2$ and $Rb_3H(SeO_4)_2$. The heat capacities of TRHSe and its deuterated analogue are measured to examine whether or not the measurement gives certain information to the phase transition. The result will be compared to that of Raman scattering.

Crystal Growth

The compound of $Rb_3H(SeO_4)_2$ were synthesized by the reaction:



The crystal of $Rb_3H(SeO_4)_2$ was grown by the slow evaporation method from the aqueous solution containing the mixture of Rb_2SeO_4 (wt 40%) and concentrated selenic acid H_2SeO_4 (wt 20%). $Rb_3D(SeO_4)_2$ was prepared by successive recrystallization from D_2O solution containing $Rb_3H(SeO_4)_2$ (Fukai *et al.*, 1992).

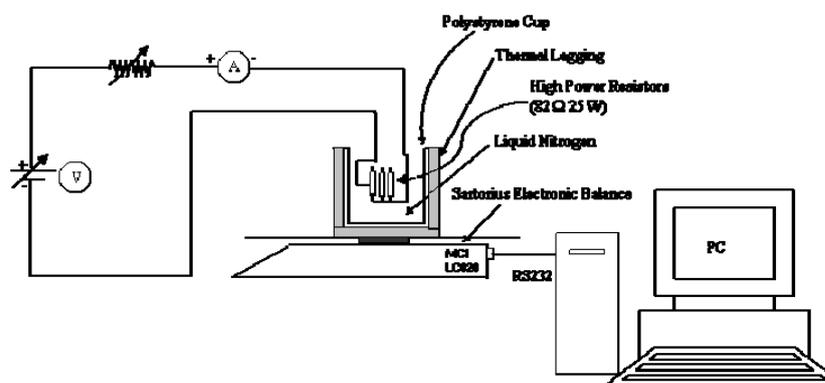


Figure 1 Block diagram of apparatus

Heat Capacity

Firstly, the latent heat L of liquid nitrogen (LN2) is measured and then this result is used to determine the specific heat (C_p) of the crystal. Having obtained L , there are three steps to be done.

- (1) About 25g of liquid nitrogen (LN2) in a polystyrene cup (lagged to prevent water freezing on its outer surface) is placed on a top loading balance (Sartorius balance) together with 3.26 grams of crystal whose heat capacity is to be determined. A small piece of thread is attached to the crystal. A top loading balance which can interface directly with a personal computer (PC) will be used. The computer can reset the balance to zero and read directly the load on the balance.
- (2) Heat is supplied by lowering the crystal into the LN2. The layout of the experimental setup is shown in Figure 2.

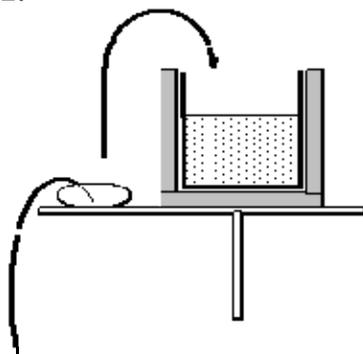


Figure 2 Layout of the experimental setup

- (3) At the thermal equilibrium between LN2 and the crystal, the computer continues to collect the mass loss data of LN2 for same time.

The value of C_p obtained is taken to be the average heat capacity in the temperature range from 77K to T_0 (Kittle & Kroemer, 1980).

Raman Scattering

The internal mode of SeO_4^{2-} does not depend on the scattering geometry, because the site symmetry of the ions is C_1 . Hence, Raman scattering was carried out in the back scattering geometry with incident and scattered lights perpendicular to the crystalline c^* plane. Spectrometer was R2000 (Raman spectrometer with green laser diode). Temperature of a specimen was measured with Pt-100 resistance thermometer and controlled within ± 1 K during measurement by the use of a cold finger cryostat.

The apparatus shown schematically in Figure 3 allows measurements down to about 80K by utilizing, a thermally conducting rod of copper as a "cold finger", which thermally links the sample and a liquid nitrogen (LN2) bath. Operation of the heating coil when LN2 is in the Dewar allows variation of the sample temperature (Thomson & White, 1983).

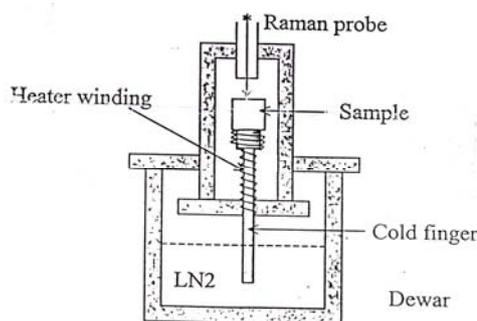


Figure 3 Cold finger cryostat

Results and Discussion

Thermal capacity

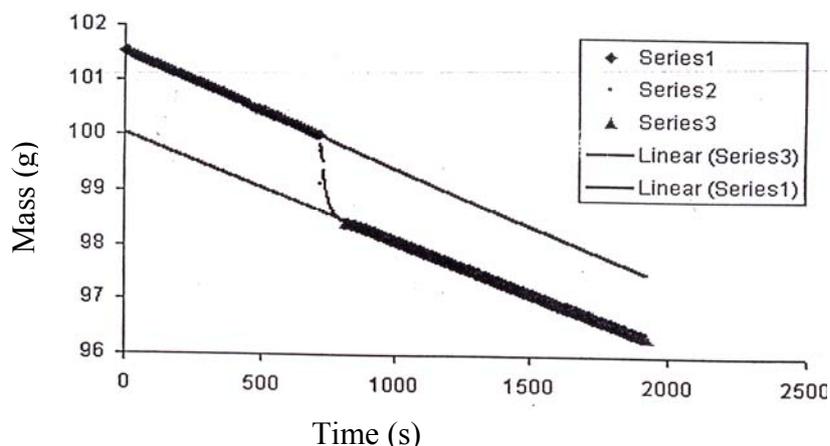


Figure 4 Plot of data for weight of cup plus $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ and LN2 as a function of time

Figure 4 is an example print out of the weight of the cup plus crystal and LN2 as a function of time obtained for TRHSe with regression fits made to the two halves of the curve before and after the crystal was added.

The specific heat capacity for sample can be calculated:

$$M\bar{C}_p (T_0 - 77) = \Delta m L$$

where M is the mass of the sample used and \bar{C}_p is the average value for C_p between room temperature T_0 and 77K.

The heat capacities of $\text{Rb}_3\text{H}(\text{SeO}_4)_2$ and $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ are calculated.

$$\text{Latent Heat of LN2} = L = 197.7 \text{ J g}^{-1}$$

$$\text{Mass of crystal} = M = 3.26 \text{ g}$$

$$\text{Atomic mass of crystal} = 545 \text{ g mol}^{-1}$$

$$\text{Initial Temperature} = T_0 = 302 \text{ K}$$

$$\text{Final Temperature} = 77 \text{ K}$$

$$\text{Mass of LN2 lost} = \Delta m = 1.49 \text{ g}$$

$$\text{Hence, } \bar{C}_p = 218.6 \text{ J mol}^{-1}\text{K}^{-1} \text{ for } \text{Rb}_3\text{H}(\text{SeO}_4)_2$$

Similarly, \bar{C}_p of $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ can be obtained as $223.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

Raman scattering

The temperature dependence of ν_2 mode for $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ is shown in Figure 5. A weak line appears on the higher frequency side of the strong single line with decreasing temperature. It increases in intensity and splits into a doublet (DL_2). In addition to this doublet, the strong single line itself also splits into a doublet (DL_1). Therefore, DL_1 and DL_2 are assigned to DSeO_4^{2-} and SeO_4^- , respectively, because of their mass difference. In the disordered phase, a deuterium in a deuterium bond moves between two wells of a double minimum potential in the bond. Hence, two SeO_4^{2-} in a dimer are equivalent in the paraelectric phase as a result of a long time average. However, they become non-equivalent

in the antiferroelectric phase because of the order of deuterium. As a result, Raman frequencies of internal modes of a SeO_4^{2-} ion change from those of $[\text{SeO}_4^{2-} - \text{D} - \text{SeO}_4^{2-}]^{3-}$ to those of SeO_4^{2-} and DSeO_4^{2-} and these lines can be separately observed.

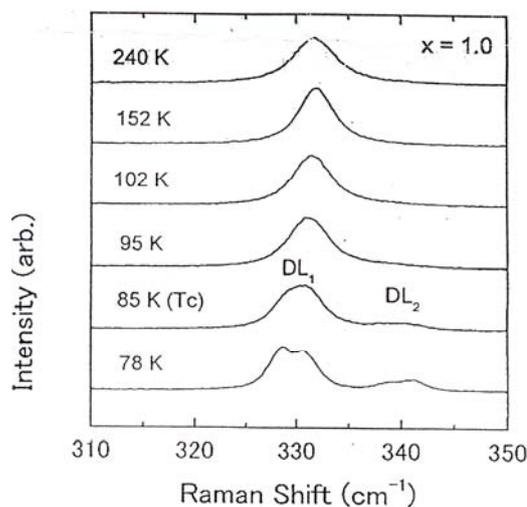


Figure 5 The temperature dependence of the ν_2 spectra of $\text{Rb}_3\text{D}(\text{SeO}_4)_2$

Conclusion

Specific heat capacity \bar{C}_p of TRHSe is $218.6 \text{ J mol}^{-1} \text{ K}^{-1}$ while that of its deuterated analogue is $223.5 \text{ J mol}^{-1} \text{ K}^{-1}$. The \bar{C}_p of $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ is slightly larger than that of TRHSe. The ν_2 mode of $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ in the paraelectric phase splits into two lines at 90K. From these facts, it is included that antiferroelectric-paraelectric phase transition of $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ occurred in the temperature below 90K.

Acknowledgements

I would like to thank Dr. Mya Mya Win, Professor and Head of the Department of Physics, Hinthada University, for her permission to undertake this paper. I would also like to express my sincere thanks to Daw Aye Ye, Professor, Department of Physics, Hinthada University, for her valuable discussion in preparing this work. I owe a great deal of thanks to my colleagues at Physics Department, Hinthada University, for all of their coordination and cooperation in this paper.

References

- Fukai, M., Matsuo, T. and Suga, H. (1992). Calorimetric study of the deuteration effect on the phase behaviour in $\text{Rb}_3\text{H}(\text{SeO}_4)_2$, *Solid State Comm*, **84** (5): 545-549.
- Kittle, C. and Kroemer, H. (1980). *Thermal Physics*. Freeman, New York.
- Thomson, C. W. and White, H. W. (1983). Latent heat and low-temperature heat capacity experiment for the general physics laboratory. *American Journal of Physics*, **51** (4): 362-364.