PHASE TRANSITION OF $(TEA)_2ZnCl_4$ SINGLE CRYSTALS STUDIED BY RAMAN

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The signal crystal of $(TEA)_2ZnCl_4$ have attracted much interest due to various structural transformations, which belong to tetragonal symmetry[1,2]. For $(TEA)_2MCl_4$-type crystals, very few Raman analysis has been performed[3]. A typical Raman spectrum of $(TEA)_2ZnCl_4$, as shown in Fig. 1, contains several features, and they are: (1)the external vibration modes below 100 cm^{-1} (2) the vibration modes of the $ZnCl_4^{-2}$ anions between 100 cm^{-1} and 350 cm^{-1} (3) the vibration modes of the TEA^+ cation above 350 cm^{-1}[4]. We will discuss our experimental results according to this classification.

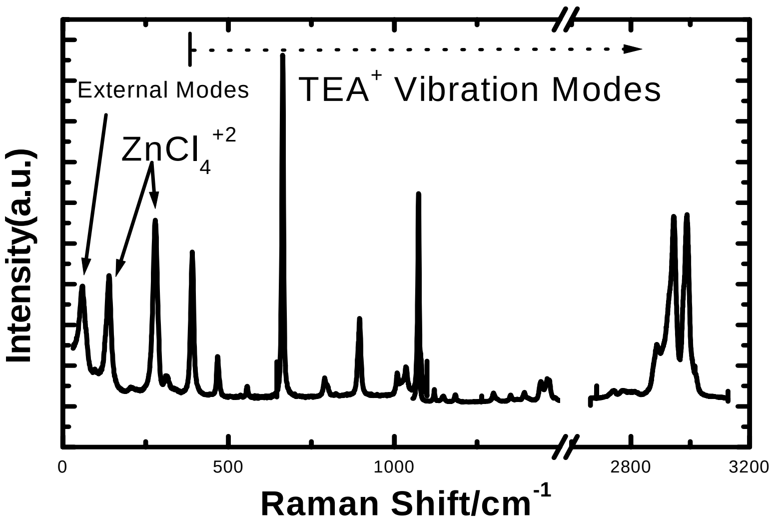

Fig. 1: Typical Raman spectrum of $(TEA)_2ZnCl_4$ single crystal.

The phase transition temperature of $(TEA)_2ZnCl_4$ signal crystal is known at 215K ~ 225K[1,2]. In Fig. 2(a), the external vibrations of cooling process is plotted, it does show the phase transition temperature is near 220 K, and splitting of Raman peaks are found below this temperature. Similar to the analysis of external mode, the internal vibration modes of the $ZnCl_4^{-2}$ anions in between 100cm^{-1} and 350 cm^{-1} also show the Raman-peak splitting due to the structure of TEA^+ ions. In Fig. 2 (b), the Raman shift of the A_1 modes of $ZnCl_4^{2+}$ is plotted against temperature and six split peaks are found at temperature lower than phase transition temperature.

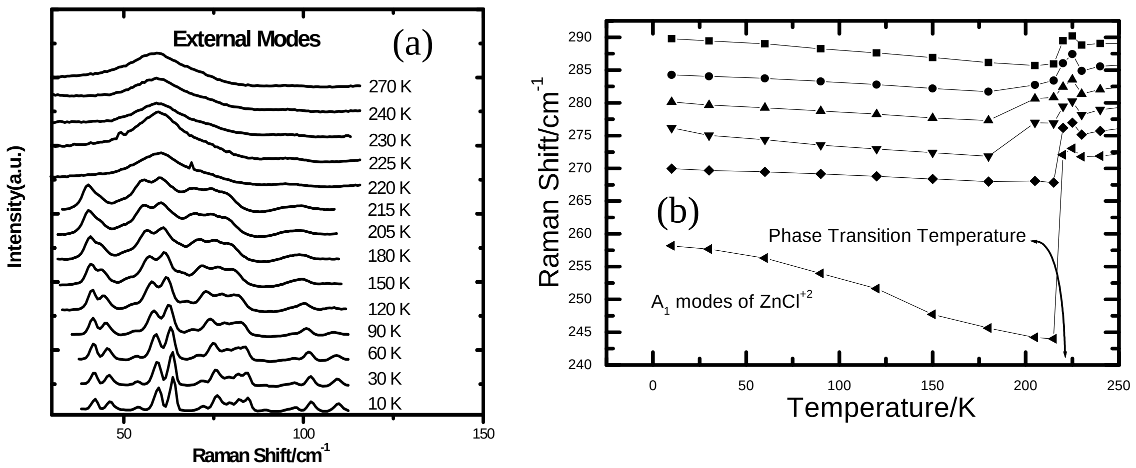

Fig. 2:Temperature-dependent Raman spectra of external modes, (a) and Raman shifts of the A1 modes of $ZnCl^{2+}$ anions (b).

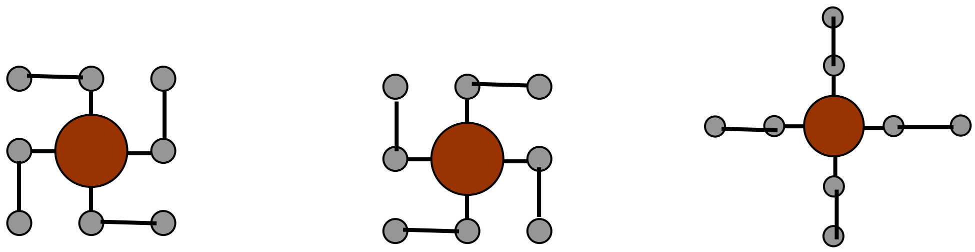

Fig. 3: The structure diagram of three different TEA^{+1} ions.

Two different structures of TEA^{+1} ions are found before[1,4]. One is an all-trans conformation (tt.tt), and this is called Greek cross. The other is a trans-gauche arrangement for Et-N-Et moiety (tg.tg), also called Nordic[1,4]. We believe that the three kind structure of TEA^{+} cation, as plotted in Fig. 3, cause the splitting of the Raman spectrum at low temperature; i.e. two (tg.tg.) and one (tt.tt). The co-existence of three different TEA^{+1} in crystal have six combinations which make the A_1 modes of $ZnCl_4^{2+}$ split into six at low temperature. The coexistence of Greek and Nordic crosses of TEA^{+} ion can be found at low temperature Raman spectra, which confirms our prediction.

1. A. J. Wolthuis, W.J. Huiskamp, L.J. DeJongh, and R.L. Carlin, Physica. 142B, 301(1986).
2. A. Mahoui, J. Lapasset, J. Moret and P.S. Gregire, Acat Cryst, C52 2671(1996).
3. T. S. Jung, H.L. Liu and J.T. Yu, Chinese J. Phys. 39, 344(2001).
4. C. Naudin, F. Bonhomme et al, J. Raman Spectrosc, 31,979-985(2000).