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## Behaviour of NTE Material $\text{Ag}_3[\text{Co}(\text{CN})_6]$ under Pressure

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**Abstract.** Recent discovery of colossal negative thermal expansion (NTE) behaviour in Silver Hexacyanocobaltate  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  has triggered interest among researchers to understand the basic mechanism causing such an unusual behaviour. This report presents our results on the behaviour of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  using *in-situ* high pressure Raman and FTIR spectroscopy. The reported trigonal-monoclinic phase transition occurring in this compound is observed at 0.2 GPa. Upon increasing the pressure further,  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  becomes irreversibly amorphous above 13 GPa.

### 1. Introduction

Negative thermal expansion materials have got practical applications in making composites where zero or very low coefficient of thermal expansion (CTE) is required. To make advancement in this applicability, however it is very important to understand the behaviour of these materials with respect to changes from ambient conditions. Research has progressed in this area after the recent discoveries of isotropic NTE property in framework materials like  $\text{ZrW}_2\text{O}_8$  [1],  $\text{Zn}(\text{CN})_2$  [2] along with many dicyanometallates [3, 4] and many metal-organic frameworks (MOFs). These structures have many low energy rigid unit modes (RUMs) which can be observed spectroscopically as soft modes with negative Grüneisen parameters [2,5]. It is found that in these structures, bridging arrangement of atoms offers greater flexibility as the constraint is only on the metal atom distances. Many of these materials exhibit pressure-temperature dependent phase transitions and also pressure induced amorphization (PIA) [6, 7].

Recently silver hexacyanocobaltate  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  was shown to have colossal anisotropic negative thermal expansion with a CTE having magnitude much larger than that of many NTE materials including  $\text{ZrW}_2\text{O}_8$  [8,9].  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  is a framework material assembled from highly under constrained Co-CN-Ag-NC-Co linkages. Its crystal structure consists of alternating layers of  $\text{Ag}^+$  and  $[\text{Co}(\text{CN})_6]^{3-}$  ions, stacked parallel to the unique axis of its trigonal  $P\bar{3}Im$  unit cell. Within any given silver containing layer, the Ag atoms are arranged at the vertices of a Kagome lattice with the

octahedral  $[\text{Co}(\text{CN})_6]^{3-}$  ions positioned above and below the hexagonal Kagome holes. This compound behaves like a garden fencing where a contraction along *c*-direction is coupled to an expansion along *a*-direction. The compound also exhibits a negative linear compression (NLC) [9]. It is understood that the flexible framework structure along with the Ag...Ag argentophilic interactions give rise to such an unusual NTE effect [10, 11]. Present work is aimed for getting better insight for the high pressure behaviour of the compound pertaining to its NLC property and also to look for possible pressure induced amorphization (PIA). Hence *in-situ* high pressure Raman, FT infrared spectroscopic investigations have been carried out and the data is presented in accordance to our current understanding.

## 2. Experimental Details

White polycrystalline  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  was synthesized by mixing aqueous solutions of  $\text{K}_3[\text{Co}(\text{CN})_6]$  and  $\text{AgNO}_3$  following precipitation as described in literature [8]. The sample was characterized by infrared spectroscopy as well as X-ray diffraction.

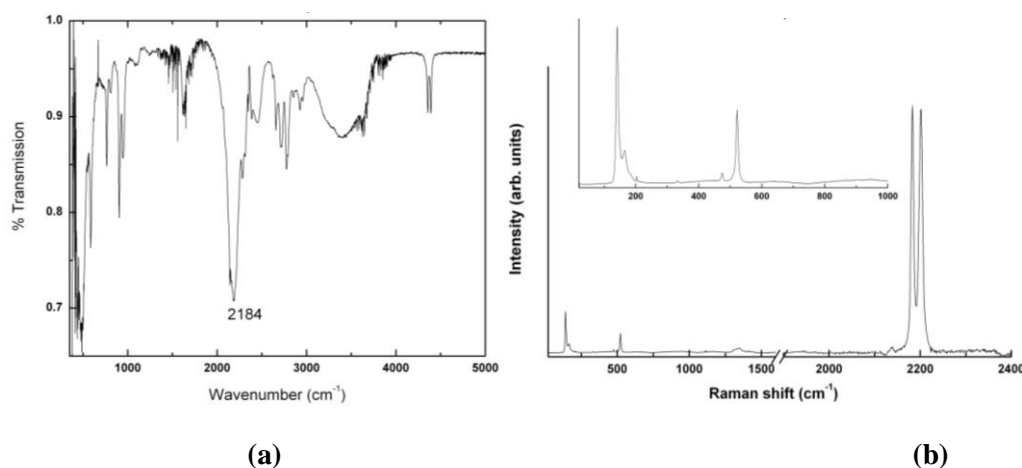
*In-situ* high pressure micro-Raman scattering measurements were done using a Jobin Yvon HR460 single stage monochromator and diode pumped frequency doubled solid state laser (532 nm) was used for excitation. Non-hydrostatic pressure Raman measurements were carried out without any pressure transmitting medium. High pressure was generated using a Mao Bell type diamond anvil cell (Diacell Lever DAC-Mega). *In-situ* quasi-hydrostatic pressure transmission spectra were recorded using Bruker's VERTEX 80V Fourier transform infrared spectrometer attached with a HYPERION 2000 infrared microscope and a mid-infrared globar source. High pressure was generated using a symmetric diamond anvil cell equipped with CVD grown synthetic diamonds. The sample was prepared by making a homogeneous mixture of 2%  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  in CsI. The spectra were recorded using liquid nitrogen cooled HgCdTe (MCT) detector. The pressure calibration in both Raman as well as IR experiments was done by ruby fluorescence technique [12].

## 3. Results and Discussion

At ambient conditions  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  exists in trigonal phase  $\text{Ag}_3[\text{Co}(\text{CN})_6]$ -I in space group  $P\bar{3}1m$ . This phase has centre of symmetry and consists of three interpenetrating distorted cubic networks having  $\text{CoC}_6$  octahedra at the cube vertices and edges formed by approximately linear  $-\text{CN}-\text{Ag}-\text{NC}-$  linkages. At 0.2 GPa, the compound is shown to undergo a structural phase transition from trigonal to monoclinic phase (space group  $C2/m$ ),  $\text{Ag}_3[\text{Co}(\text{CN})_6]$ -II accompanied by a very large volume change  $\Delta V/V=16.25\%$  [9].

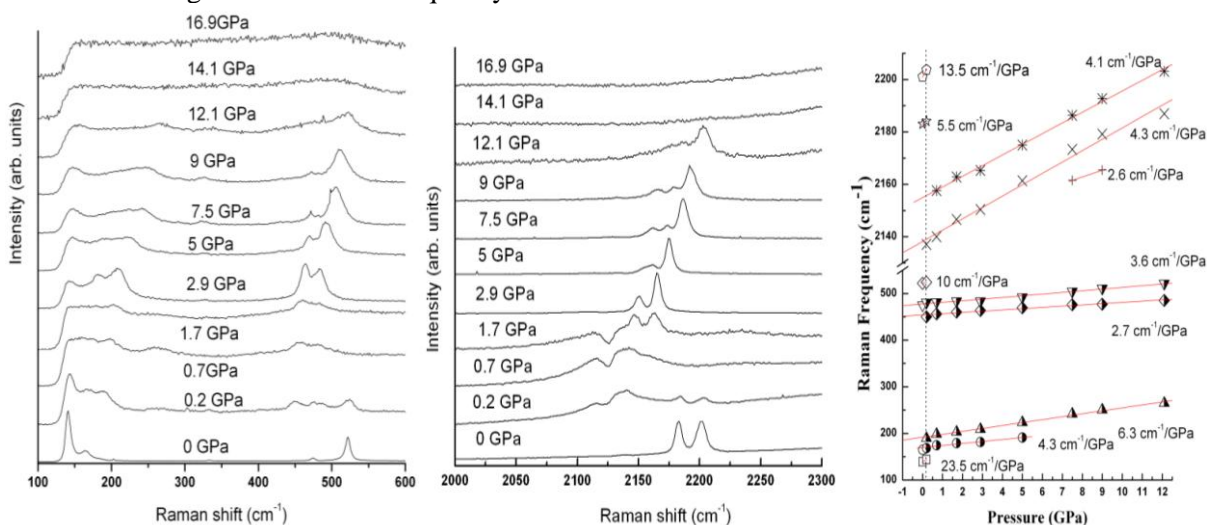
Owing to its centrosymmetric structure, Raman and infrared active modes are mutually exclusive. To our best knowledge, there are no reports on group theoretical calculations for  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  to explain the normal modes of vibration. Since  $\text{H}_3[\text{Co}(\text{CN})_6]$  is isostructural [13] to the compound of present study, direct correlation has been drawn from the vibrational modes of  $\text{H}_3[\text{Co}(\text{CN})_6]$  [14] and with comparison to that of  $\text{K}_3[\text{Co}(\text{CN})_6]$  [15]. Figure 1(a) shows infrared spectrum and 1(b) shows Raman spectrum of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  recorded at ambient conditions. The infrared spectrum shows a strong mode at  $2184\text{ cm}^{-1}$  corresponding to  $\text{C}\equiv\text{N}$  stretching vibrations. Also, there are modes observed at  $581\text{ cm}^{-1}$  corresponding to  $\text{Co}-\text{C}\equiv\text{N}$  bending and two sharp modes in  $4000\text{ cm}^{-1}$  region which are mainly combination of  $\text{C}\equiv\text{N}$  stretching Raman and IR active modes. Apart from these modes, there are several modes observed between  $760-950$  and  $2300-2950\text{ cm}^{-1}$ , some of which may be combination modes. Ambient Raman spectrum of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  shows strong modes at  $139, 165, 475$  and  $522\text{ cm}^{-1}$  corresponding to  $\text{C}-\text{Co}-\text{C}$  deformation,  $\text{N}-\text{Ag}-\text{N}$  bending,  $\text{Ag}-\text{N}$  stretching and  $\text{Co}-\text{C}$  stretching respectively. Two very strong modes appear at around  $2183\text{ cm}^{-1}$  and  $2201\text{ cm}^{-1}$  corresponding to  $\text{C}\equiv\text{N}$  stretching. All these observed mode frequencies match well with the expected mode frequencies and

with those reported in recent study [16], (Table 1). The evolution of Raman modes with increasing non-hydrostatic pressure up to 17 GPa is shown in Figure 2. The compound becomes amorphous around 13 GPa and the process of amorphization is found to be irreversible. There are significant changes in the spectra around 0.2 GPa at which  $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-II}$  is formed.



**Figure 1 :** Vibrational Spectra of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  at ambient conditions (a) Infrared spectrum (b) Raman spectrum

The mode at  $139\text{ cm}^{-1}$  could not be traced beyond 0.2 GPa whereas the one at  $165\text{ cm}^{-1}$  increases in frequency with pressure. The Co-C stretching  $522\text{ cm}^{-1}$  mode disappears at 0.2 GPa and a new mode at  $481\text{ cm}^{-1}$  appears. The two  $\text{C}\equiv\text{N}$  stretching modes at  $2183\text{ cm}^{-1}$  disappear at 0.2 GPa and two new modes appear at lower frequencies at around  $2140\text{ cm}^{-1}$  and  $2158\text{ cm}^{-1}$  which harden with pressure. One more peak appears at  $2162\text{ cm}^{-1}$  around 7.5 GPa. This may be associated with puckering of silver atoms in the 2-D lattice leading to a triangular network [9]. To our observation, none of these modes show negative pressure dependence. It was difficult to trace a peak at  $335\text{ cm}^{-1}$  due to Co-C $\equiv$ N bending in our data due to poor signal to noise ratio. Interestingly, this peak has been observed to show negative pressure dependence by a recent study [16]. The variation of Raman mode frequencies with pressure are shown in Figure 2 and the values of the slopes  $d\omega/dP$  for each of the modes are mentioned alongside each mode frequency variation shown with linear fits.

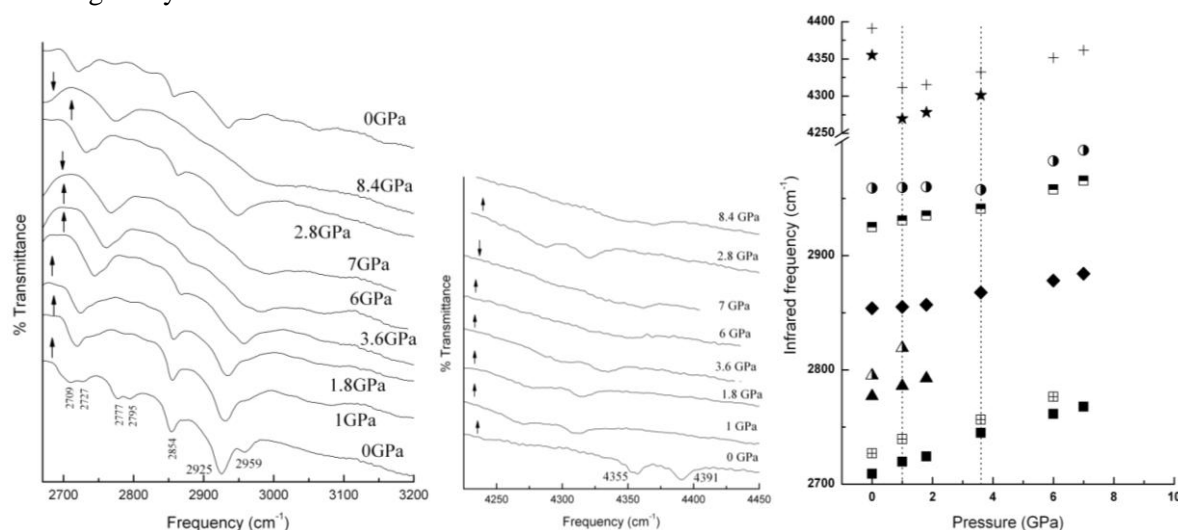


**Figure 2:** Raman spectra of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  recorded under non-hydrostatic pressure environment and variation of Raman mode frequency with pressure

$\nu$ ( $\text{cm}^{-1}$ )	Vibration	$\nu$ ( $\text{cm}^{-1}$ )	Vibration
(R) 139	C-Co-C deformation	(IR) 760-950	Combination modes
(R) 165	N-Ag-N bending	(IR) 2184	C $\equiv$ N stretching
(R) 475	Ag-N stretching	(R) 2183, 2201	C $\equiv$ N stretching
(R) 522	Co-C stretching	(IR) 2300-2950	Combination modes
(IR) 581	Co-C $\equiv$ N bending	(IR) 4000	Combination of C $\equiv$ N stretching R & IR modes

**Table 1:** Observed vibrational frequencies in  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  at ambient conditions

Before we discuss the results of in-situ high pressure infrared spectroscopy, we would like to point out that the C $\equiv$ N stretching vibrational mode around  $2185 \text{ cm}^{-1}$  does get shifted to around  $2128 \text{ cm}^{-1}$  along with red shift of all the other IR modes at ambient conditions if the sample is prepared by mixing of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  with other transparent matrix like KBr [17, 18]. There are two possibilities to understand this: (1) the pressure of 0.2 GPa required to transform  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  –I to  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  –II can easily be achieved while preparing the sample for IR experiments. If this phase transition is irreversible then it is hard to study this compound using such matrix materials for IR measurements. (2) In case of KBr matrix, small traces of water in the title compound can facilitate exchange of Ag and K producing AgBr and  $\text{K}_3[\text{Co}(\text{CN})_6]$  for which the C $\equiv$ N stretching mode appears at  $2128 \text{ cm}^{-1}$ . Note that our high pressure IR measurements refer to evolution of the spectrum with pressure for which ambient IR spectrum does show the C $\equiv$ N peak shift to  $2128 \text{ cm}^{-1}$ . CsI, being less reactive than KBr, the second of the above possibility seems too rare. So presently, we are inclined to conclude that the effect is related to the formation of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  –II due to hand driven pressure in mortar and pestle. In order to completely rule out the second possibility, we would like to carry out our experiments with  $\text{CaF}_2$  as a matrix which is negligibly reactive as compared to KBr and CsI. The ambient IR spectrum of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  does not show the peak shift to  $2128 \text{ cm}^{-1}$  as it is measured on nascent  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  compound in CsI (without any grinding) by DRIFT method. Figure 3 shows the behaviour of vibrational modes with pressure as studied by micro FTIR experiments. Modes only above  $2700 \text{ cm}^{-1}$  could be followed due to limitation of MCT detector and strong absorption in  $2000 \text{ cm}^{-1}$  region by the diamonds.



**Figure 3:** Pressure dependence of FTIR spectra of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  and IR mode frequencies

The pressure in IR run was increased to 7 GPa. The compound was then decompressed to 2.8 GPa and again pressurized to 8.4 GPa. Finally the pressure was completely released. To our surprise, we found that the structure of  $\text{Ag}_3[\text{Co}(\text{CN})_6]$  –II is quite flexible and shows almost complete reversibility except some hysteresis in the mode frequencies. With pressure, all the modes in  $2700\text{--}3200 \text{ cm}^{-1}$  region show

positive pressure dependence. The original modes in 4000 cm<sup>-1</sup> region which are combinations of IR and Raman active C≡N stretching vibrations still exist in the sample filled inside DAC at lowest pressure and two new modes appear on lower frequency side which are very weak may be due to diamond absorption. With increase in pressure, the original modes lose their intensity and the new modes exhibit positive pressure dependence. Figure 3 shows pressure variation of IR mode frequencies. The rest of the modes show a marked change in pressure dependence  $d\omega/dP$ , at around 3.6 GPa. The reason for this slope change needs to be understood.

A detailed study of our *in-situ* high pressure infrared as well as X-ray diffraction results is in progress.

#### 4. Conclusion

We have studied behaviour of polycrystalline Ag<sub>3</sub>[Co(CN)<sub>6</sub>] under non-hydrostatic pressure environment using Raman and under quasi-hydrostatic pressure environment using FTIR spectroscopy spanning the pressure range across both the phases of Ag<sub>3</sub>[Co(CN)<sub>6</sub>]. This compound shows irreversible amorphization above 13 GPa. We didn't notice negative pressure dependence for any of the observed vibrational modes and more detailed study needs to be done in this regard. We also observed flexibility in the structure of Ag<sub>3</sub>[Co(CN)<sub>6</sub>] –II from our high pressure FTIR data. It would be of importance to know if any of the observed modes can be related to Ag...Ag argentophillic interactions.

#### 5. Acknowledgement

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#### 6. References

- [1] Mary T A, Evans J S O, Vogt T and Sleight A W 1996 *Science* **272** 90
- [2] Goodwin A L and Kepert C J 2005 *Phys. Rev. B* **71** 140301(R)
- [3] Goodwin A L, Kennedy B J and Kepert C J 2009 *J. Am. Chem. Soc.* **131** 6334
- [4] Korcok J L, Katz M J and Leznoff D B 2009 *J. Am. Chem. Soc.* **131** 4866
- [5] Zwanziger J W 2007 *Phys. Rev. B* **76** 052102
- [6] Perotoni C A and da Jornada J A H 1998 *Science* **280** 886
- [7] Catafesta J, Haines J, Zorzi J E, Pereira A S and Perotoni C A 2008 *Phys. Rev. B* **77** 064104
- [8] Goodwin A L, Calleja M, Conterio M J, Dove M T, Evans J S O, Keen D A, Peters L and Tucker M G 2008 *Science* **319** 794
- [9] Goodwin A L, Keen D A and Tucker M G 2008 *Proc. Natl. Acad. Sci. USA* **48(105)** 18708
- [10] Goodwin A L, Keen D A, Tucker M G, Dove M T, Peters L and Evans J S O 2008 *J. Am. Chem. Soc.* **130** 9660
- [11] Conterio M J, Goodwin A L, Tucker M G, Keen D A, Dove M T, Peters L and Evans J S O 2008 *J. Phys.: Condens. Matter* **20** 255225
- [12] Forman R A, Piermarini G J, Barnett J D and Block S 1972 *Science* **176**, 284
- [13] Pauling L and Pauling P 1968 *Proc. Natl. Acad. Sci. USA* **60** 363
- [14] Haser R, Bonnet Band Rozere J 1977 *J. Mol. Struct.* **40** 177
- [15] Jones L H 1962 *J. Chem. Phys.* **36** 1209
- [16] Rao R, Achary S N, Tyagi A K and Sakuntala T 2011 *Phys. Rev. B* **84** 054107
- [17] Kob N E and House Jr J E 1994 *Trans. Met. Chem.* **19** 31
- [18] Reguera E, Quintana G and Fernandez-Bertran J 1997 *Trans. Met. Chem.* **22** 527