Raman spectroscopic investigations on delafossite CuLaO$_2$ at high pressures

Nilesh P. Salke$^1$, Rekha Rao$^{1,*}$, S. N. Achary$^2$, A. K. Tyagi$^2$

$^1$Solid State Physics Division, Bhabha Atomic Research Center, Mumbai – 400085, India
$^2$Chemistry Division, Bhabha Atomic Research Center, Mumbai – 400085, India

E-mail: rekhar@barc.gov.in

Abstract. Vibrational properties of delafossite CuLaO$_2$ are investigated using Raman spectroscopy at ambient conditions and at high pressures. Changes are observed in the Raman spectrum at around 1.8 GPa which could be related to a phase transition. The changes observed are reversible from 7 GPa.

1. Introduction

Transparent conducting oxides (TCO) of the delafossite family AMO$_2$ ($A =$ Cu, Ag; $M =$ Al, Ga, In) have many technological applications in solar cells, touch panels, as electrodes in flat panel displays, ultraviolet-emitting diodes [1]. While there are many $n$-type TCOs, $p$-type conductivity found in CuMO$_2$ is rare and useful in pn junctions [2]. Recently, Copper delafossites CuMO$_2$ have also been used as photo-catalysts for hydrogen production by water splitting [3].

Delafossite type crystals have layered structure with space group $R\bar{3}m$ with general formula AMO$_2$, in which monovalent cations $A$ ($A =$ Cu, Ag) are linearly coordinated with two oxygen ions along the $c$-axis and the trivalent cations $M$ are octahedrally coordinated to oxygen atoms [4]. Earlier high pressure investigations of delafossite compounds have revealed interesting phase transitions in which Cu environment is affected whereas environment of $M$ is unchanged [5]. Both CuAlO$_2$ and CuGaO$_2$ have been reported to transform to unresolved structures above 34 and 26 GPa respectively [1,6]. CuScO$_2$ is reported to have structural transitions with pressure above 13 GPa [7]. Recent first-principles calculations determined the critical pressure of transition for CuAlO$_2$ to be 60 GPa [8].

Recently, Negative thermal expansion (NTE) has been reported in some members of this family like CuScO$_2$, and CuLaO$_2$ [4,9]. NTE is attributed to the anharmonicity of linear O-Cu-O bond along the $c$-axis, and this effect increases with increase in the size of the atom at $M$ site. Interesting fact is that CuLaO$_2$ exhibits NTE in both $a$ and $c$ edges at low temperature and it shows nearly isotropic thermal expansion though its structure is anisotropic. Neutron diffraction studies [4] have reported that the cell parameter $a$ shows positive expansion above 100 K, while $c$-parameter contracts in the temperature range 30-200 K and expands at higher temperatures upto 600 K.

High pressure Raman investigation of NTE materials often exhibits interesting phenomena like softening of phonons, phase transitions and also amorphization. Raman spectroscopic studies at high pressures often exhibit interesting phenomena like softening of phonons, phase transitions and also amorphization.
pressures gives information about the mode Grüneissen parameter, which is useful for understanding the thermal expansion behavior. It has been observed that in most of the NTE materials, strong vibrations perpendicular to some interatomic bond plays an important role; such as O-Cu-O bond in Cu$_2$O. Though Raman spectroscopy gives information about only the zone-center phonons, it is quite useful in understanding the contribution of different vibrations to the thermal expansion. Here we report Raman spectroscopic studies of high pressure behavior of CuLaO$_2$.

2. Experimental details
The compound CuLaO$_2$ was synthesized by solid state reaction of Cu$_2$O and La$_2$O$_3$. Raman spectroscopic measurements at high pressure were carried out from inside a diamond anvil cell Diacell B-05 with 4:1 methanol-ethanol mixture as pressure transmitting medium. Spectrum of polycrystalline sample was excited using 532 nm line of power $\sim$15 mW. Pressure was measured using the ruby fluorescence technique. Scattered light was analyzed using a home built 0.9 m single monochromator, coupled with an edge filter and detected by a cooled CCD. Entrance slit was kept at 50 $\mu$m, which gives a spectral band pass of 3 cm$^{-1}$.

3. Results and Discussions
In the delafossite structure R$ar{3}$m, primitive unit cell consists of 4 atoms resulting in 12 normal modes which transform as $r = A_{1g} + E_g + 3A_{2u} + 3E_u$. Movement in the direction of Cu-O bonds along the hexagonal c axis is represented by $A$ modes, whereas $E$ modes correspond to vibrations in the perpendicular direction. $3A_{2u} + 3E_u$ are IR active modes which include acoustic modes ($A_{2u} + E_u$). $E_g$ and $A_{1g}$ are Raman active modes. In the absence of single crystals, Raman modes were identified using the Raman spectra of analogous compounds [1,6].

![Raman spectra of CuLaO$_2$ at ambient conditions](image)

Figure 1 shows the Raman spectra of CuLaO$_2$ at ambient conditions (Phase PI). It consists of two modes at 318 and 652 cm$^{-1}$ identified as $E_g$ and $A_{1g}$ respectively. Both the frequencies are lower than that of other delafossites due to higher La mass and weaker La-O bonds. $E_g$ mode is more intense than $A_{1g}$. In addition, several features of intensity comparable to that of $A_{1g}$ mode were also observed. Such features in other delafossites were attributed to defect induced modes (due to Cu vacancies or interstitial oxygen) which appear due to relaxation of selection rules and were identified by abinitio calculations[1,6].
Figure 2 shows the Raman spectra at various pressures. Both the Raman modes increase monotonically with pressure. Above 1.8 GPa, new modes appear in the low frequency region and the $E_g$ mode shows splitting. With further pressurization one of the split components of $E_g$ showed softening. Appearance of new modes and changes in the pressure dependencies of mode frequencies indicate a phase transition to a phase PII. Above 1.8 GPa, the $A_{1g}$ mode could not be followed. With further pressurization, Raman intensity drastically reduced above 7 GPa. Pressure coefficients of the Raman modes is 5.5 cm$^{-1}$/GPa for $E_g$ and 9.5 cm$^{-1}$/GPa for $A_{1g}$ mode in phase PI. Appearance of many new modes in PII indicates lower symmetry of the high pressure phase. Nature of changes observed at 1.8 GPa is similar to the transition observed in other delafossite members CuAlO$_2$ and CuGaO$_2$ which transform at 34 and 26 GPa respectively [1,6].

![Figure 2. Raman spectra of CuLaO$_2$ at various pressures. Note the appearance of new modes above 1.8 GPa.](image)

The Cu-O bond length decreases and unit cell edge $a$ increases with ionic radius of the $M^{3+}$ ion in this class of compounds. The variation in the transition pressure can be correlated to the ionic radii of trivalent cation which is coordinated octahedrally to oxygen atoms. We observe that the transition pressure $P_c$ is inversely proportional to the ionic radius of $M$ in this class of delafossites CuMO$_2$. Figure 3 gives the relation between transition pressure of the delafossites to the ionic radii of octahedrally coordinated trivalent cation.
4. Conclusion

High pressure behaviour of CuLaO$_2$ is investigated up to 7 GPa, beyond which Raman modes could not be followed due to abrupt decrease in intensity. The compound exhibits a phase transition at 1.8 GPa similar to the phase transitions observed in CuAlO$_2$ and CuGaO$_2$ at 34 and 26 GPa respectively.

5. References

[1] Pellicer-Porres J, Martinez-Garcia D, Segura A, Rodriguez-Hernandez P, Munoz A, Chervin J C, Garro N and Kim D 2006 Phys. Rev. B 74 184301
[2] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H and Hosono H 1997 Nature (London) 389 939
[3] Huda M N, Yan Y and Al-Jassim M M 2011 J App. Phys 109 113710
[4] Li J, Sleight A W, Jones C Y and Toby B H 2005 J. Solid State Chem. 178 285
[5] Pellicer-Porres J, Segura A, Ferrer-Roca Ch, Martinez-Garcia D, Sans J A, Martinez E, Itie J P, Polian A, Baudelet F, Munoz A, Rodriguez-Hernandez P and Munsch P 2004 Phys Rev B 69 024109
[6] Pellicer-Porres J, Segura A, Martinez E, Saitta A M, Polian A, Chervin J C and Canny B 2005 Phys. Rev. B 72 064301
[7] Gilliland S, Pellicer-Porres J, Segura A, Muñoz A, Rodríguez-Hernández P, Kim D, Lee M S and Kim T Y 2007 phys. stat. sol. (b) 244 No. 1 309–314
[8] Nakanishi A and Katayama-Yoshida H 2011 J Phys Soc Japan 80 024706
[9] Ahmed S I, Dalba G, Fornasini P, Vaccari M, Rocca F, Sanson A, Li J and Sleight A W 2009 Phys. Rev. B 79 104302

Acknowledgement

Nilesh P. Salke acknowledges Department of Atomic Energy, India for financial support. The authors thank Dr. S. L. Chaplot for support and encouragement.