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► To cite this version:

Jacky Even, Laurent Pedesseau, Olivier Durand, M. Modreanu, G. Huyberechts, et al.. Vibrational properties of SrCu₂O₂ studied via Density Functional Theory calculations and compared to Raman and infrared spectroscopy measurements. European Materials Research Society Spring Meeting 2012 (E-MRS Spring 2012), May 2012, Strasbourg, France. pp.113-116, 10.1016/j.tsf.2012.10.130 . hal-00805323

HAL Id: hal-00805323

<https://hal.science/hal-00805323v1>

Submitted on 28 Mar 2013

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Vibrational properties of SrCu₂O₂ studied via DFT calculations and compared to Raman and infrared spectroscopy measurements

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Abstract.

The SrCu₂O₂ material is a p-type Transparent Conductive Oxide (TCO). A theoretical study of the SrCu₂O₂ crystal is performed with a state of the art implementation of the Density functional theory (DFT). The simulated crystal structure is compared with available X-ray diffraction data and previous theoretical modelling. Density functional perturbation theory (DFPT) is used to study the vibrational properties of the SrCu₂O₂ crystal. A symmetry analysis of the optical phonon eigenvectors at the Brillouin zone center is proposed. The Raman spectra simulated using the derivatives of the dielectric susceptibility, show a good agreement with Raman scattering experimental results.

Keywords: DFT, SrCu₂O₂, X-ray scattering, Raman spectroscopy.

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1. Introduction

SrCu_2O_2 is a p-type transparent conductive oxide (TCO) [1-3] which is combining high electrical conductivity and optical transparency, like in n-type TCO. TCO materials are used for electrostatic shielding, antistatic screens, transparent heating devices, solar cells and even organic light emitting diodes [3, 4]. The vibrational properties of SrCu_2O_2 crystal are only reported in a few experimental papers, but vibrational spectroscopy could offer a very interesting alternative for material characterisation [5]. Most theoretical studies focus indeed on the electronic properties, band structures or acceptor defects [5-11]. The origin of the transparency was also investigated systematically in related compounds $\text{A}^{\text{II}}\text{Cu}_2\text{O}_2$ where $\text{A}^{\text{II}}=\text{Mg, Pb, Ca, Ba, Sr}$.

In this paper, a theoretical study of the SrCu_2O_2 crystal is performed with a state of the art implementation of the Density functional theory (DFT). The simulated crystal structure is in reasonable agreement with available X-ray diffraction data. Density functional perturbation theory (DFPT) is used to study the vibrational properties of the SrCu_2O_2 crystal. A symmetry analysis of the optical phonon eigenvectors at the Brillouin zone center is proposed. Born charge tensors are determined for each atom. The Raman spectra simulated using the derivatives of the dielectric susceptibility, is compared with Raman scattering experimental results.

2. Experimental and computational details

Ceramics of SrCu_2O_2 were synthesized by reacting a stoichiometric mixture of Cu_2O (99.5%) and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ for 40 h in a nitrogen flow at 950 °C. The reaction product was ground and hot pressed into a pellet by at 975 °C.

The room temperature Raman measurements have been performed in a backscattering geometry using a Jobin Yvon /Horiba LabRam spectrometer equipped with a N₂-cooled CCD detector, and the 488 nm Ar⁺ laser line as excitation.

The theoretical study of SrCu₂O₂ is performed using the Density Functional Theory (DFT) implementation available in the ABINIT package [12]. A local density approximation (LDA) is used for the exchange-correlation functional [13]. Norm-conserving pseudopotentials are constructed for Sr [4s²4s⁶5s²], Cu [3d¹⁰4s¹] and O [2s²2p⁴] atoms in a standard format [14] using the OPIUM code [15]. These valence configurations are similar to the ones used in previous DFT simulations of the ground state [5-11] and give a good description of the conduction band and valence band edges close to the band gap [5-11]. A plane-wave basis set with an energy cut-off of 950 eV is used to expand the electronic wave-functions. The reciprocal space integration is performed over a 12x12x12 Monkhorst-Pack grid [16]. Energy convergence is accurately reached with tolerance on the residual potential which stems from difference between the input and output potentials. The crystal structure has been relaxed until the forces acting on each atom are smaller than 5.10⁻⁵eV/Å.

The so-called 2n+1 theorem [17] within the DFPT provides a direct access to the second and third-order response function and has been used for the vibrational analysis of various materials [18-20]. A DFPT implementation is available in the ABINIT package [12] but a LDA must be used for the exchange-correlation functional in the ground state computation.

3. Results and discussion

3.1 Vibrational modes at Γ point

3.1.1 Symmetry analysis

SrCu₂O₂ exhibits a tetragonal structure (space group $I4_1/amd$ or D_{4h}^{19}) with two formula units per unit cell. In this crystal structure, the Sr atoms are at the center of a distorted octahedron formed by O atoms. The ten atoms of the primitive cell give rise to 30 zone center vibrational modes. The Sr, Cu and O atoms are in special Wyckoff positions 4a, 8d and 8e with site symmetry D_{2d} (or $-42m$), C_{2h} (or $2/m$) and C_{2v} (or mm), respectively. From the correlation method [21], we can identify the species of the site group for each lattice vibration and correlate these species with the D_{4h} factor group species.

The irreducible representations relative to the lattice vibrations involving the Sr atoms are

$$\Gamma_{Sr} = A_{2u} + B_{1g} + E_u + E_g ,$$

those involving the Cu atoms are

$$\Gamma_{Cu} = A_{1u} + 2A_{2u} + B_{1u} + 2B_{2u} + 3E_u ,$$

and those involving the O atoms are

$$\Gamma_O = A_{1g} + A_{2u} + B_{1g} + B_{2u} + 2E_u + 2E_g .$$

After subtraction of the three acoustic modes ($A_{2u} + E_u$) of the total representation of the crystal, the irreducible representations associated with the vibrational modes are

$$\Gamma = A_{1g} + A_{1u} + 3A_{2u} + 2B_{1g} + B_{1u} + 3B_{2u} + 5E_u + 3E_g,$$

where A_{1g} , B_{1g} and E_g are Raman-active modes, A_{2u} and E_u are IR-active modes, the other modes being silent. Thus, six Raman lines and eight IR lines are expected in the spectra. Concerning the IR spectra, it should be noted that the A_{2u} modes involve atom displacements parallel to the z axis whereas in E_u modes, they are perpendicular to the z axis. As for the Raman modes, the A_{1g} mode involves only O atom displacements and the Cu atoms are motionless.

3.1.2 Dielectric tensors

The Z_{ij} Born charge tensors for each atom have been calculated via DFPT in the SrCu_2O_2 crystal lattice. These tensors reflect the sites symmetries and form the basis of the computation of the dielectric constants and dynamical matrix. Table I shows the results for the phonon ϵ_{\bullet}^{ion} and electronic $\epsilon_{\bullet}^{\infty}$ contributions to the total static dielectric constants ϵ_{\bullet}^s . The phonon contribution to the static dielectric constant is large, especially along the z axis. The anisotropy of the static dielectric constant is then mostly related to this contribution.

3.1.3 Comparison to Infrared spectroscopy for polar modes

A previous experimental study by infrared spectroscopy [5] has shown peaks located either in the far-infrared spectral range at 123, 147 and 251 cm^{-1} or in the mid-infrared spectral range, with a strong peak at 578 cm^{-1} and a shoulder at about 600 cm^{-1} . This observation is compared to the theoretical calculation.

Our DFPT calculations provide peaks located at 39.0 cm^{-1} (E_u), 106.9 cm^{-1} (E_u), 124.6 cm^{-1} (A_{2u}), 135.0 cm^{-1} (E_u), 225.8 cm^{-1} (A_{2u}), 248.0 cm^{-1} (E_u), 608.2 cm^{-1} (E_u), and 626.5 cm^{-1} (A_{2u}). In fact, this calculation reveals two new modes which are not observed yet at 39.0 cm^{-1} and probably the one at 106.7 cm^{-1} . The high frequency modes observed at 578 cm^{-1} and 600 cm^{-1} might be assigned to the computed E_u (608.2 cm^{-1}) and A_{2u} (626.5 cm^{-1}) ones, but extensive studies by infrared spectroscopy should be performed, particularly using light polarization in order to get a precise mode assignment. We also note that there is a tendency to overestimate the frequencies of the modes, both for polar and unpolar modes (see section 3.2.1).

3.2 Comparison to Raman scattering experiments for unpolar modes

3.2.1 Experimental results

In a previous study, microRaman mapping of a bulk polycrystalline SrCu_2O_2 target has already revealed features located at 188, 236, 286 and 530 cm^{-1} assigned to Raman active modes for the tetragonal phase of SrCu_2O_2 [5]. A new study of a carefully polished SrCu_2O_2

sample (figure 1) shows features located at 112, 133, 156, 183, 230, 286, 455, 497, 524, 584 and 687 cm^{-1} . The peaks at 183, 230, 286 and 524 cm^{-1} correspond to the results quoted in the previous study. The shoulder observed at 497 cm^{-1} was also present in the spectrum shown in ref. [5]. A spectrum of a Cu_2O powder obtained under the same experimental conditions sample shows (figure 1) features located at 114, 126, 150, 179, 191, 200, 220, 288, 332, 412, 480 and 620 cm^{-1} .

Indeed, our DFPT calculations provide the Raman peaks located at 124.5 cm^{-1} (E_g), 154.7 cm^{-1} (E_g), 186.2 cm^{-1} (B_{1g}), 513.9 cm^{-1} (E_g), 557.1 cm^{-1} (B_{1g}), and 558.2 cm^{-1} (A_{1g}). So, we do not get any mode within the interval from 200 to 480 cm^{-1} which is definitively belonging to the CuO_2 crystal. X-ray diffraction (not shown here) has confirmed the presence of a Cu_2O polycrystalline extra-phase in the SrCu_2O_2 pellet studied in the present paper. Such an additional phase was not present in the following study reported in ref [5], and may be due to a slight variation of the elaboration conditions.

We may then conclude that the shoulder located at 497 cm^{-1} and the strong peak 524 cm^{-1} (figure 1) can be attributed to the polycrystalline SrCu_2O_2 sample. In the low frequency range (below 230 cm^{-1}), the vibrational modes of SrCu_2O_2 are mixed with vibrational modes attributed to a residual Cu_2O powder used for the synthesis of the materials. Concerning the two modes at 236 and 286 cm^{-1} previously attributed to the SrCu_2O_2 lattice, they are very similar to those observed in Cu_2O and are probably oxygen-related vibration modes identical in both crystal structures.

Figure 2 is schematic illustrations of the eigenvectors associated to Raman active optical mode calculated at frequencies equal to 558.2 cm^{-1} (A_{1g}). The Cu atoms are not represented. Only four slices at $z=0, 1/4, 1/2,$ and $3/4$ are needed to correctly represent the crystal as defined in ref. [1]. For the A_{1g} mode (figure 2), O atoms vibrate only along the z

axis. Some O atoms vibrate in phase opposition with other O atoms located in the same crystalline layer.

3.2.2 Simulation of Raman spectra

The Raman susceptibility α^{ν} tensors for a given vibrational eigenmode ν have been calculated following standard definitions [12, 22, 23]:

$$\alpha_{ij}^{\nu} = \sqrt{\Omega} \sum_n \sum_l \left. \frac{\partial \chi_{ij}}{\partial r_l} \right|_n \frac{\xi_{nl}^{\nu}}{\sqrt{m_n}} \begin{cases} n \equiv \text{Sr, Cu, O} \\ i, j, l \equiv x, y, z \end{cases}$$

where Ω is the volume of the primitive cell, χ_{ij} is the dielectric susceptibility tensor, r_l is the displacement of n along the Cartesian axes, m_n is the mass of n , and ξ_{nl}^{ν} the normalized eigenmode of the atom n in the vibrational mode ν . The calculation of the Raman susceptibility requires knowledge of the derivatives of the dielectric polarization tensor which is the more demanding computational part. The three derivatives (Table III) of the dielectric polarization tensors of Cu atom are equal to zero (see section 4.2.1). The Raman susceptibility tensors were computed for light polarizations parallel (V) and orthogonal (H) to the incident one. HH and HV Raman spectra were then calculated considering polycrystalline samples (figure 3). The spectra are shown over the entire [0-700 cm^{-1}] energy range on the left part of the figure. Three peaks are located at low energy whereas the three others are close to each others, two of them being almost degenerated (A_{1g} and B_{1g} modes). The right part of figure 3 shows that the A_{1g} mode is very sensitive to polarizations contrary to the other one. A tentative interpretation of the experimental results (figure 1) can be proposed. The shoulder located at 497 cm^{-1} could be attributed to the high frequency E_g mode (513.9 cm^{-1}) whereas the strong peak at 524 cm^{-1} could correspond to the sum of the almost degenerated high frequency A_{1g} (558.2 cm^{-1}) and B_{1g} (557.1 cm^{-1}) modes. A better agreement between computed and experimental frequencies may be obtained by refining the DFPT computation,

either by using an improved exchange-correlation functional or by taking into account core electrons into the electronic configurations for the atoms. More, a better agreement could be expected taking into account temperature induced shifts of vibrational frequencies. Theoretical frequencies are indeed computed by DFT at $T=0\text{K}$, whereas experiments are only available up to now at room temperature.

4. Conclusion

In summary, this paper presented a theoretical analysis of the mechanical structure, and vibrational properties of SrCu_2O_2 crystal lattice. A first DFPT computation of the dynamical matrix at the Brillouin zone center is proposed. The Born charges and the dielectric tensors are calculated and the Raman scattering spectra is simulated. Additional Raman measurements of SrCu_2O_2 and Cu_2O samples are performed. A tentative assignment of non-polar vibrational high frequency modes is proposed for SrCu_2O_2 .

Acknowledgments

The ab initio simulations have been performed on HPC resources of CINES and IDRIS under the allocation 2012-[x2012096724] made by GENCI (Grand Equipement National de Calcul Intensif).

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Figure captions:

Figure 1: Experimental Raman spectra of Cu_2O powder and polycrystalline SrCu_2O_2 at room temperature.

Figure 2: Representation of the SrCu_2O_2 A_{1g} normal mode at $z=0, \frac{1}{4}, \frac{1}{2},$ and $\frac{3}{4}$.

Figure 3: DFT HH and HV Raman spectra of SrCu_2O_2