

THz Vibrational Modes of Halide Double Perovskite Cs₂AgBiBr₆ at Band Gap Resonance

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Cs₂AgBiBr₆ is a member of the halide double perovskite family with high photovoltaic efficiency. We have synthesized single crystals of Cs₂AgBiBr₆ from solution using a controlled cooling method. The THz vibrational modes near band gap resonance were investigated by temperature dependent Raman scattering, supplemented by optical transmission measurements of the band gap itself. With a 532.8 nm laser the mode at 5.36 THz shows a very strong resonance peaked at 30 K.

INTRODUCTION

Materials with high photovoltaic efficiencies are of interest due to their application in a wide range of optical devices. Lead-based halide perovskites have high photovoltaic efficiencies but tend to be thermally unstable due to the presence of an organic group and are not ideal for applications due to the toxicity of lead. Cs₂AgBiBr₆ is a member of the halide double perovskite family and has been proposed as a more stable and less toxic alternative while retaining high photovoltaic efficiency[1]. This halide double perovskite also has a high defect tolerance having little change in the free carrier density with an increase in lattice defects[1].

The discovery of halide double perovskites as potential high photovoltaic efficient materials is relatively recent and has produced an area of active optical investigation. With the goal of better understanding the photovoltaic properties of these materials, we have studied optical transmission and resonant Raman scattering of Cs₂AgBiBr₆. Large single crystals were obtained through a controlled cooling method[2] where crystals are grown by dissolving the components in a heated acidic solution and manually controlling the rate of cooling in a furnace in order to reduce the number of nucleation sites.

RESULTS

Powders of CsBr, BiBr₃, and AgBr, mixed in a molar ratio of 2:1:1, were added to HBr acid and heated at 95°C until dissolved to produce a solution of 0.08M molarity. Controlled cooling in a furnace yielded crystals with typical dimension 3-4 mm.

The crystals were characterized via powder and single crystal X-ray Diffraction (XRD) using a Rigaku XRD system. The optical surface was found to have [1,1,1] orientation. The phase transition from the low temperature tetragonal structure (I4/m) to the room temperature cubic structure (Fm-3m) was detected as an endothermic feature at around 120 K upon warming via differential scanning calorimetry (DSC) as shown in the inset to Fig. 3.

Raman scattering spectroscopy was carried out using a Montana Instruments Microveval Raman system with a

532.8 nm (2.327 eV) laser at a power of 0.1 mW. The single crystal sample was cooled down to 3.5 K and warmed in steps of 5 K from 5 K to 300 K. As shown in Fig. 1 due to the laser being close in energy to the band gap of Cs₂AgBiBr₆ a strong photoluminescent background was observed as well as resonance of the phonons in the THz regime.

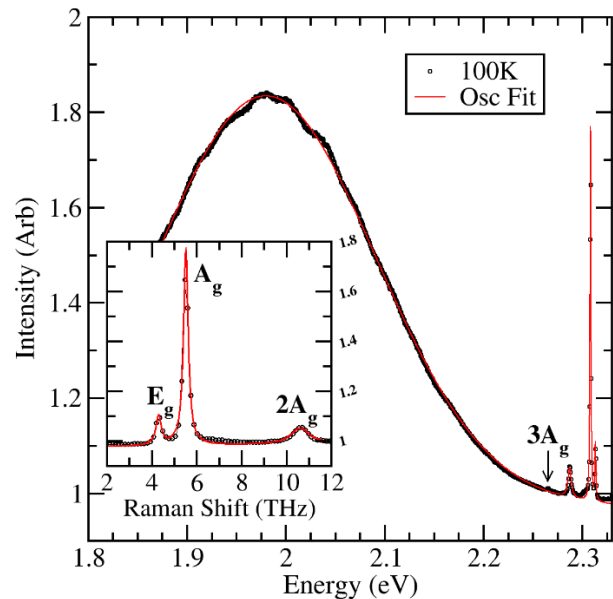


Fig 1. Resonance Raman scattering spectrum measured at 100K displaying Raman active vibrational modes superimposed on a strong photoluminescent background with the phonon peaks fitted to Lorentzian oscillators and the photoluminescence background fitted to a Gaussian. Note that the very weak third order Ag mode is not included in the fit. The inset shows a detail of the phonon spectrum plotted as Raman shift.

The band gap of Cs₂AgBiBr₆ was measured via optical transmission using a UV to NIR grating spectrometer with Xenon arc-lamp as light source, an optical high wavelength pass filter to attenuate second order light and a lock-in amplifier with an external chopper to measure the signal from the photovoltaic detectors used. With the aid of a Tauc plot, the band gap at room temperature was found to be indirect with a magnitude of 1.95 eV in agreement with the results of Shade *et.al.* [3]. The energy maximum of the photoluminescent background (see Fig. 1) corroborates this result since the electron-hole pairs recombine from energy levels near the conduction band minimum to the levels near the valence band maximum. With a relatively low band gap, Cs₂AgBiBr₆ thus has the potential to utilize light from the infrared to the ultraviolet in photovoltaic applications.

As observed in Fig 1. four phonon peaks appear in the resonance Stokes Raman scattering near 4.25 THz (142 cm⁻¹), 5.36 THz (179 cm⁻¹), 10.58 THz (353 cm⁻¹), and 15.74 THz

(525cm^{-1}) corresponding to the E_g , A_g , and second and third order A_g Raman active vibrational modes in the tetragonal phase and E_g , A_{1g} and its second and third order overtones in the cubic phase respectively[4]. Two additional lower frequency Raman active modes with group symmetry F_{2g} , predicted from a group theoretical analysis and observed in Reference [4] could not be investigated since they are below the range of our instrument. The observation of second and third order overtone modes is the result of strong electron-phonon Fröhlich interactions[5].

Since at higher temperatures the photoluminescence background became broader, overlapping heavily with the THz phonon region, it was fitted to a Gaussian curve in order to extract the temperature dependence of the phonon modes, which were fitted using a series of Lorentzian oscillators (see Fig. 1). The most intense phonon mode was the A_{1g}/A_g mode at 5.36 THz exhibiting strong resonance behavior with maximum enhancement near 30 K (Fig. 2).

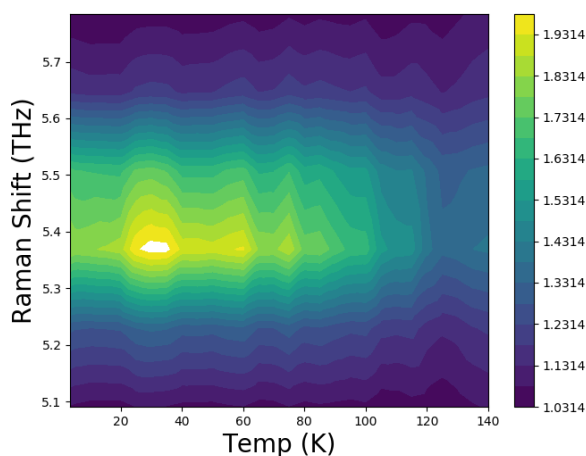


Fig. 2. Resonance Raman scattering of the 5.36 THz vibrational mode of $\text{Cs}_2\text{AgBiBr}_6$ as a function of Raman Shift and temperature with intensity in arbitrary units displayed as false color. Note that the resonance has a maximum near 30 K.

The intensity, center frequency, and half width at half max (HWHM) of the 5.36 THz A_g phonon obtained from the fit are plotted as a function of temperature in Fig. 3. The transition from the low temperature tetragonal phase of $\text{Cs}_2\text{AgBiBr}_6$ to the high temperature cubic phase near 120K causes anomalies (marked by arrows) in the temperature dependence of the parameters.

Note that the center frequency of the 5.36 THz A_g phonon begins to harden with decreasing temperature below 40 K suggesting this is another characteristic temperature for $\text{Cs}_2\text{AgBiBr}_6$. Anomalies are also observed at this temperature in the fitting parameters of the photoluminescent background. Similar halide double perovskites exhibit a second, lower temperature phase transition. Rb_2KScF_6 , for example, undergoes the structural phase transition from cubic to tetragonal as temperature decreases and then a second phase transition from tetragonal to monoclinic. It is however unlikely that this feature at 40 K in $\text{Cs}_2\text{AgBiBr}_6$ is due to a second structural phase transition since it is not observed in DSC data or in the temperature dependent X-ray scattering[3] results for the lattice parameters, cell volume, and spontaneous strain. The

origin of the anomalous behavior at 40 K remains to be investigated further.

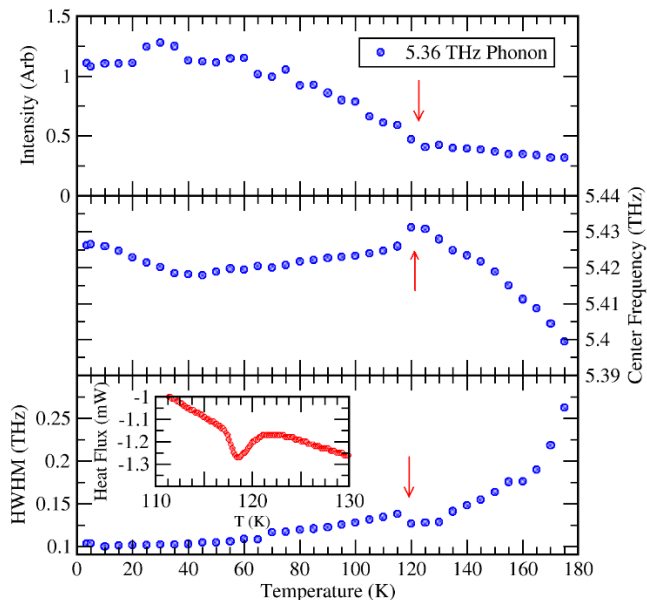


Fig. 3. Lorentzian fitting parameters as a function of temperature for the 5.36 THz phonon. The transition from the low temperature tetragonal phase to the cubic phase is evident from anomalies near 120 K indicated with arrows. The inset in the lower panel shows the phase transition measured with DSC.

SUMMARY

The Stokes Raman spectrum of $\text{Cs}_2\text{AgBiBr}_6$ has been investigated in the THz regime and found to exhibit resonant enhancement with 532.8 nm incident laser excitation. In addition to resonant behavior, the A_{1g}/A_g phonon at 5.36 THz exhibits anomalies in the temperature dependence of its Lorentzian fit parameters at the cubic/tetragonal structural phase transition near 120 K as well as at a lower characteristic temperature of 40 K whose origin remains to be determined.

ACKNOWLEDGEMENTS

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