Raman Spectra of Bismuth Oxyhalide Single Crystals

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Oxyhalogenides of bismuth BiOX (X=Cl, Br and I) are very interesting materials which find various applications as X-ray luminescent screens, anti-Stokes (frequency upshift) converters, luminophors, and photoconducting analyzers of linear polarized radiation. Since each primitive cell consist of six monoatomic sites, the structure of the reduced representation of the 15 normal modes of vibration is: $\Gamma = 2A_{1g}(Ra.) + B_{1g}(Ra.) + 3E_g(Ra.) + 2A_{2u}(i.r.) + 2E_u(i.r.)$, in which the vibrations of A_{1g}, B_{1g} and E_g species are active in the Raman spectrum and those of A_{2u} and E_u species are active in the infrared (i.r.) spectrum. The Raman active modes are observed in frequency range $55 - 225$ cm^{-1}, $50 - 185$ cm^{-1}, and $45 - 175$ cm^{-1} for the BiOCl, BiOBr and BiOI single crystals respectively.

1. Introduction

When light (photons) interacts with a crystal, there are several processes that take place simultaneously. Light can be reflected, refracted, absorbed and finally the light can be elastically and inelastically scattered. The Raman effect refers specifically to the inelastic scattering of photons. In the case of crystals, this inelastic dispersion is due to interaction between the photons and the vibrations of the crystal lattice with a change in the polarizability induced by the incident radiation. This interaction depends on the symmetry of these vibrations, or phonon modes.

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The Raman spectral data of single crystal bismuth oxyhalides have not yet been extensively studied. In the present study, the Raman active vibrational fundamentals of the single-crystalline bismuth oxyhalides are discussed using the results of the factor group analysis. The optically active normal vibrations are discussed by comparison with the results of the calculations of phonon spectra in terms of rigid ion model.

In this paper we present the results of a Raman investigation of such crystals.

2. Experimental details

The BiOX single crystals were grown by the chemical gas transport reactions method in the closed volume (typically of the order 10x10x0.5 mm^3). They crystallize in the tetragonal matlockite (PbFCl) type structure (space group $D_{4h}^7 - P\frac{4}{n}mm$; $Z = 2$). The trivalent Bi^{3+} ion is surrounded at one side by four oxygen ions and at the other side by five halide ions, four of which are in a plane, whereas fifth is situated on the fourfold axis. There is only one crystallographic site available for the trivalent ion. This site has C_{4v} symmetry.

BiOX samples were characterized by X-ray diffraction. The lattice parameters of the crystals were refined by using Si internal standard (high purity) and by the least square method.

The spectra have been recorded with the DFS 6 monochromator spectrometer equipped with a spectra physics He-Ne 50 mW laser. The spectral slit-width was 1 cm^{-1}.

The crystals was oriented by means of goniometric device. The polarization planes of the incident and scattered light was controlled by a half-wave plate. The light was collected at 90°.
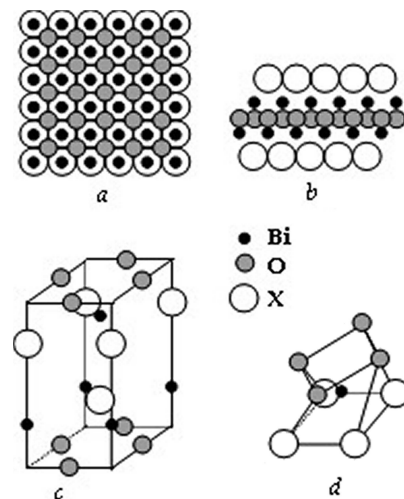

Fig. 1. Crystal structure of bismuth oxyhalides: (a) projection to (001) plane; (b) projection to (100) or (101) plane; (c) clinographic projection of the unit cell; (d) coordination polyhedron of the bismuth.

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3. Results, discussion and conclusion

A BiOX Laue photograph, taken parallel to the large face of the platelets, showed clearly a fourfold symmetry axis characterizing (001) planes of a matlockite tetragonal PbFCl-like structure $D_{4h}^7 - P\frac{4}{n}mm$ (No. 129) with two formula units in the unit cell.

Figure 1a shows the clinographic projection of the unit cell of BiOX crystals. Each Bi atoms is eight-coordinated by four O atoms and four X (halogen) atoms in the form of an asymmetric decahedron [1]. Each atom (Bi, O, X) occupies a special position with multiplicity 2. The faces of the decahedron are 2 rectangles (O-O-O-O, X-X-X-X, which are parallel to the (110) plane and 8 isosceles triangles (four X-O-X and four O-X-O). The decahedra are linked to each other by a common O-X edge along the a and b axes, forming infinite layers. The coordination of O and X is as follows: each O atom is linked to four Bi atoms, forming a tetragonal pyramid with the O atom at its apex. Also each X atoms forms with the neighbouring Bi atoms a tetragonal pyramid with the X atom at its apex. Neighbouring decahedra form layers along (001) which are connected by common O-X edges. Neighbouring layers of decahedra are connected by common O-O or X-X edges.

The X atom is bonded with four Bi atoms in a planar square to form a pyramid and with its nonbonding (lone pair) electrons pointing to the other side of the square. These nonbonding electrons convert the three-dimensional fluorite-like structure into a two-dimensional layered structure. In the three-dimensional Bi_2O_3, the Bi atoms are coordinated to six O atoms. This structural difference between them is the major reason for BiOX to have a wider optical band-gap. Therefore, the BiOX single crystals can be described as 2D structured materials.

Since each primitive cell consist of six monoatomic sites, the structure of the reduced representation of the 15 normal modes of vibration is:

$$\Gamma = 2A_{1g}(Ra.) + B_{1g}(Ra) + 3E_g(Ra) +$$

$$2A_{2u}(i.r.) + 2E_u(i.r),$$

in which the vibrations of A_{1g}, B_{1g} and E_g species are active in the Raman spectrum and those of A_{2u} and E_u species are active in the infrared (i.r.) spectrum. There are no optically inactive fundamentals. In the present Raman investigation, however, only five fundamental bands were found for the BiOCl, BiOBr and BiOI.

The spectra in Fig. 2 are shown for several orientations of the polarization planes. The Raman active modes are observed in frequency range $55 - 225$ cm^{-1}, $50 - 185$ cm^{-1}, and $45 - 175$ cm^{-1} for the BiOCl, BiOBr and BiOI single crystals respectively.

The observed extinctions allow the direct discrimination between the doubly degenerate modes of E_g symmetry and the symmetrical ones of A_{1g} and B_{1g} type.
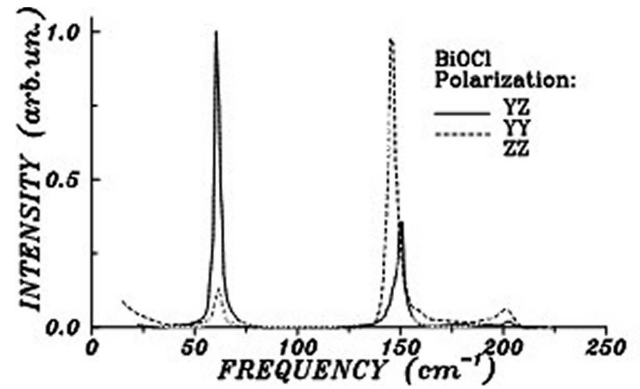

Fig. 2. Raman spectra of the BiOCl single crystal.

Raman frequencies of BiOCl.   TABLE

	E_g	A_{1g}	E_g	A_{1g}	B_{1g}
Powder	58	-	144	200	-
Crystal	59.5	144.5	150	201.5	-
Single crystal	**59.7**	**144.3**	**150.2**	**201.8**	**-**
Atoms in movement	Bi,O,Cl	Bi,Cl	Bi,O,Cl	Bi,O	O

Table gives the proposed assignments for the observed frequencies for BiOCl.

Only three peaks were observed in the Raman spectrum of the powder, but the single crystal data shows that the $144.3 - 144.5$ cm^{-1} peak corresponds to the overlapping of the two modes, one A_{1g} and one E_g. We find five fundamentals only, out of a total of six predicted by the factor group analysis.

We compare the spectra corresponding to the two orientations Z(XX)Y and X(ZZ)Y, and notice that the intensity of the 201.8 cm^{-1} peak is considerably lower for the first orientation. We may thus conclude that this peak is not of B_{1g} symmetry.

The oxygen atoms only are allowed to move during the B_{1g} vibration, because of the symmetry conditions related to this type of vibrations [1]. Experiments show that neither the 144.4 nor the 201.8 cm^{-1} peak exhibit this type of behaviour.

References

[1] V. Bunda, S. Bunda, *Superconductors – properties, technology, and applications* ISBN: 978-953-51-0545-9, Eds. Yu. Grigorashvili, InTech, Rijeka (Croatia) 2012, p. 323.