A Raman Study Of Order-Disorder Phenomena In $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ Compounds

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Abstract. A Raman study of order-disorder phenomena in the diluted magnetic semiconductors $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ series ($0 \leq x \leq 1$) is presented. The end compounds ZnGa_2Se_4 and MnGa_2Se_4 crystallize in the $\bar{I}42m$ and $\bar{I}4$ space groups respectively, presenting either partial cation disorder ($\bar{I}42m$) or total cation order ($\bar{I}4$). In this work, a relation between the shape of a mode at $\nu \approx 180 \text{ cm}^{-1}$ and the degree of cation order has been found. This band can be decomposed in a narrow and a broad component, related with the long range order and local non periodicity respectively. Cation ordering has been seen to increase after a heating treatment up to 600°C and further cooling to RT.

Keywords: Diluted magnetic semiconductor; Raman scattering, cation order-disorder.

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INTRODUCTION

The $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ ($0 \leq x \leq 1$) compounds are diluted magnetic semiconductor (DMS) of the type $\text{A(II)B(III)}_2\text{C(VI)}_4$, which are characterized by the presence of crystallographically ordered vacancies. They are promising candidates for optoelectronic devices owing to their unusual combination of magnetic, optical and electronic properties [1]. Order-disorder phenomena are important because they can change the energy gap and other optical and electronic properties [2]. In this work we present a Raman study of the $\text{Zn}_{1-x}\text{Mn}_x\text{Ga}_2\text{Se}_4$ system, focusing on the relation between the shape of some modes and the degree of cation order.

MnGa_2Se_4 crystallizes in the $\bar{I}4$ space group (s.g.) with a completely ordered cation distribution [3]. ZnGa_2Se_4 presents a partial cation disorder ($\bar{I}42m$ s.g.) with half of the Ga atoms and the Zn atoms sharing a crystallographic site [4]. RT neutron diffraction has shown that for $x < 0.5$ the structure is partially disordered with $\bar{I}42m$ s.g., while for $x > 0.5$ the materials show cationic order with $\bar{I}4$ s.g. [5]

EXPERIMENTAL DETAILS

Single crystals have been produced by the chemical vapor transport (CVT) technique, using iodine as a transport agent. Two series of samples have been

studied: as grown ones (AG), which were fast cooled from 850°C to RT, following the standard CVT procedure, and samples that have been heated under vacuum to 600°C and then furnace cooled to RT, which will be called after-heated samples (AH).

Raman Spectra have been collected in backscattering geometry onto a (112) plane with incident and scattered electric field parallel to a $\langle 110 \rangle$ direction and excitation at 514.53 nm . Power at the sample was $\approx 1 \text{ mW}$, and the spectral resolution $\leq 3 \text{ cm}^{-1}$.

EXPERIMENTAL RESULTS

Group theory predicts 13 and 12 Raman active modes for the $\bar{I}4$ and $\bar{I}42m$ compounds respectively, the main difference being that three totally symmetric A modes are found in $\bar{I}4$ s.g. and only two in $\bar{I}42m$. All modes have been assigned in previous works in the spectra for MnGa_2Se_4 . [6]

We shall focus in the second A mode, $A^{(2)}$ with $\nu \approx 180 \text{ cm}^{-1}$, that involves Se displacements within the tetragonal a-b plane. This mode is allowed in $\bar{I}4$ and forbidden in $\bar{I}42m$ s.g., as can be seen in fig.1 for the end compounds MnGa_2Se_4 and ZnGa_2Se_4 .

Fig.2 shows the dependence of the spectra in the region of the first two A modes, for the AG (left) and AH samples (right), respectively. It can be seen that

the $A^{(2)}$ mode increases with x in both series indicating that the order degree increases with the Mn content.

FIGURE 1. Raman spectra of the end compounds $MnGa_2Se_4$ and $ZnGa_2Se_4$.

FIGURE 2. Raman spectra of the as grown and after heated series of $Zn_{1-x}Mn_xGa_2Se_4$ in the region of A modes.

A close look at the 180 cm^{-1} mode shows that it can be decomposed into two bands, a narrow and a broad one, with opposite behavior along the series. The narrow band is present only in the $I\bar{4}$ compounds and decreases with decreasing x . The broad band increases with decreasing x and remains active in the $I\bar{4}2m$ compounds though it is formally forbidden. A lineshape fitting has been performed to quantify the amount of narrow and broad bands, as shown in fig.3. Fig 4 shows the integrated intensity of the narrow and broad bands, as a function of x . Intensities relative to that of the 135 cm^{-1} A mode are presented, since that mode was found to be weakly dependent on x , except for resonance effects, that are common to both modes.

We attribute the narrow band to long range $I\bar{4}$ cation order while the broad band is attributed to local non periodicity. In $I\bar{4}$ compounds periodicity can be broken by cation mixing or by antisite Mn occupation. The loss of periodicity in $I\bar{4}2m$ compounds is due to the inherent cation disorder, which gives rise to locally ordered domains, with cation distribution similar to that of $I\bar{4}$ compounds.

Compared to the AG samples and for the same x , in the AH ones the intensity of the narrow band increases while that of the broad band decreases, which means that an ordering process has developed in the AH samples.

FIGURE 3. Fitting of the 180 cm^{-1} band as a sum of a broad and narrow band.

From the correlation between the narrow band and the long range order, we conclude that the cation distribution can be varied in these materials upon thermal treatment. Since a correlation has been proved to exist between structural order and preferent occupation by Mn of the 2d crystallographic site of $I\bar{4}$ s.g. [5], we propose that heating to 600°C and subsequent cooling has led to a more ordered configuration, with Mn atoms tending to occupy preferently the 2d site.

FIGURE 4. Integrated intensity of the narrow and broad bands of both series as a function of x . Intensities have been normalized to that of the 135 cm^{-1} mode.

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