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An EXAFS study of the structure of the Zn$_{1-x}$Be$_x$Se alloy system

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Abstract. Zn$_{1-x}$Be$_x$Se is an interesting II-VI semiconductor showing unusual phonon behavior for 0.19<x<0.81 which has been ascribed due to presence of chains of Be and Se with two slightly differing Be-Se bond distances. EXAFS data have been recorded for several compositions of Be in this mixed crystals at the Zn and Se K edges and analyzed to determine the nearest and next nearest neighbor distances for Zn and Se atoms as a function of “x”. The effects of these chains is observed in the form of an increase in the $\sigma^2$ value of the Be-Se bond at $x = 0.42$ and 0.55 as compared to smaller “x” values of 0.06, 0.16 and 0.27. Theoretical estimates show that the bond length difference between the two Be-Se bonds is ~ 0.04 Å, which seems to be too small to be resolved as two different bond lengths but could be observed only as increase in $\sigma^2$ value for larger values of “x”. The trends in the various bond angles as a function of “x” have also been explained in terms of the distorted tetrahedral structure in the ternary.

1. Introduction

Be doped II-VI compounds are of importance due to their resistance to the propagation of threading dislocations, leading to enhanced lifetime of II-VI based blue-green semiconductor diode lasers [1]. This technologically important property has been attributed to the large shear modulus of the Be-VI bonds, eg. the shear modulus of BeSe is 42.6 GPa as compared to 18.35 GPa for ZnSe [2]. Besides its technological importance, the Raman data of this material system shows a novel and atypical three mode behavior, ie, a single mode for Zn-Se bond and a two-mode behavior for the Be-Se bond [3] in complete contradiction to the Modified Random Element Isodisplacement (MREI) model [3]. This observation has been explained by invoking the fact that the Be atoms, in the mixed crystal, can be in a Be rich domain (Be atoms connected to each other forming a chain and referred to as hard like (HL) region) and a Zn rich domain (isolated Be atom or small clusters surrounded by Zn atoms referred to as soft like (SL) region) [3]. The HL and SL regions in the system result in two different force constants for the Be-Se bonds, which show up as two different modes in the Raman data. Ab-initio calculations for the same material system have also revealed that the Be-Se bond in the HL and SL regions have slightly different bond lengths [4].

Besides the interpretation of the Raman measurements in terms of the presence of two different bond lengths and its support from ab-initio calculations, there have been no other independent measurements that confirm the presence of two different bond lengths for the Be-Se bonds. The motivation of the present work is to detect the possible existence of different Be-Se bond lengths in Zn$_{1-x}$Be$_x$Se mixed crystals. EXAFS is a very powerful tool to analyze the nearest neighbor (NN) bond lengths. Thus, in this work, we have analyzed the EXAFS data to determine the composition dependence of the nearest neighbor distances in Zn$_{1-x}$Be$_x$Se and probe the possibility of the direct observation of the different bond lengths for the Be-Se bond in these mixed crystals. Our analysis shows that the EXAFS data are consistent with the interpretation of the Raman data in terms of a two mode behavior. We have also evaluated the next nearest neighbor (NNN) bond lengths to have a detailed understanding of the atomic arrangement in this ternary compound. Although the EXAFS data of Zn$_{1-x}$Be$_x$Se crystals is qualitatively similar to those reported for other mixed systems, some distinct quantitative differences exist between Zn$_{1-x}$Be$_x$Se and other systems like Cd$_{1-x}$Mn$_x$Te[5], ZnSe$_x$Te$_{1-x}$.
GaAs$_x$P$_{1-x}$ and In$_x$Ga$_{1-x}$As[8]. Finally, the quantitative differences in the EXAFS data of this material system and other previously studied ternary systems have been examined in detail in this work. The trends in the various bond angles as a function of Be composition have also been explained in terms of the distorted tetrahedral structure of the ternary.

2. EXPERIMENTAL

Various Zn$_{1-x}$Be$_x$Se samples grown by high pressure horizontal Bridgeman technique, with “x” varying from 0.06 to 0.55, were studied [9]. The lattice parameters determined using X-Ray diffraction was found to satisfy the Vegard’s Law. The Zn and Se K edge EXAFS data were recorded at room temperature in the scanning EXAFS (SAMBA) beamline at the SOLEIL Synchrotron facility. The background removed and normalized data obtained using Athena was fitted with the EXAFS equation for the nearest (NN) and the next nearest (NNN) neighbors using FEFF 8.0 code implemented in Artemis software.

3. Results and discussion:

Fig 1 shows the Zn-Se and Be-Se bond lengths for the various samples. The stars show the values of $a(x)\sqrt{3/4}$ ($=b_{\text{vca}}$) for some of the “x” values (“x” refers to the Be composition ), where $a(x)$ is the lattice parameter determined from XRD, (identical to virtual crystal approximation value). One can clearly see that $R_{\text{Zn-Se}}$ and $R_{\text{Be-Se}}$ change very little, as the composition of Be increases from 6% to 55%. However the average lattice parameter and hence $b_{\text{vca}}$ shows a smooth variation with “x”.

A closer look at the data in fig 1 reveal s that there is a finite variation in $R_{\text{Zn-Se}}$ and $R_{\text{Be-Se}}$ with “x”. This fact has been observed in nearly all the III-V ternaries and has been quantified for GaAs$_x$P$_{1-x}$, where it was found that the two constituent bond lengths $R_{\text{Ga-As}}$ and $R_{\text{Ga-P}}$ changed linearly with “x” with the same slope $S_1$. The value of $S_1/S_1^{\text{v}}$ (where $S_1^{\text{v}}$ is the slope of the first coordination bond length described with Vegard’s law under VCA) was 18% in GaAs$_x$P$_{1-x}$ [7]. In Zn$_{1-x}$Be$_x$Se the slopes for the variation in $R_{\text{Zn-Se}}$ ($S_1^{\text{Zn-Se}}$) and $R_{\text{Be-Se}}$ ($S_1^{\text{Be-Se}}$) are different. The value of the $S_1^{\text{Zn-Se}}/S_1^{\text{v}}$ and $S_1^{\text{Be-Se}}/S_1^{\text{v}}$ is 33% and 13% respectively. This implies that the stiffer Be-Se bond distorts much less as compared to the weaker Zn-Se bond. The value of $S_1^{\text{Zn-Se}}/S_1^{\text{v}}$ is little over twice of $S_1^{\text{Be-Se}}/S_1^{\text{v}}$, which is similar to the stiffness constant ratio of bulk BeSe and ZnSe. Postinokov et.al. have evaluated the equilibrium bond lengths for some compositions of Be in Zn$_{1-x}$Be$_x$Se [4]. The values of $S_1^{\text{Zn-Se}}/S_1^{\text{v}}$ and $S_1^{\text{Be-Se}}/S_1^{\text{v}}$ estimated from the fig.3 of ref.[4] are 30.5% and 9.3% respectively, which are in close agreement with our experimental values.

Raman measurements and theoretical calculations indicate that, the stiffer Be-Se bond is expected to show a two mode behavior corresponding to its location in the hard and soft regions of the mixed crystal [3] and are ~ 2.24 Å and 2.28 Å for “x” close to the lower threshold of percolation. The fact that good fits to the $\chi(q)$ data are obtained by using a single Be-Se bond, indicates that in the present experiment, EXAFS measurements donot explicitly distinguish the presence of the two different bond lengths by the EXAFS data analysis. This is be due to the following reasons: a) Be is a weak scatterer with the consequence that the signal due to the Be atoms in the EXAFS data at the Se edge is very small, b) the presence of a large signal from Zn atoms, which are present at nearly the same distance away from the Se atoms masks the details of the Be scattering signal. These factors thus make it very difficult for us to deconvolve the two Be-Se bond lengths.

Fig 2. shows the Debye-Waller factor ($\sigma^2$), which is a measure of the static and dynamic disorder around the absorbing atom, for the Zn-Se and Be-Se bonds as a function of “x”. We find that for all the samples, the $\sigma^2$ for the Be-Se bonds is smaller than the values for the Zn-Se bonds. The value of $\sigma^2$ for the Zn-Se bond is nearly independent of “x”. This value compares well with the reported value for pure ZnSe at 300K [9] indicating that the thermal disorder has the major contribution to $\sigma^2$ as compared to the static disorder. The stiffer Be-Se bond has a much smaller value of $\sigma^2$ and hence far less distorted as compared to Zn-Se bond.
Figure 1. The NN and NNN distances as a function of “x”. The stars show the NN distance as evaluated from X-Ray data.

The interesting observation is that for x = 0.42 and 0.55, σ^2 for the Be-Se bond is comparatively larger (although smaller than the Zn-Se bond) than the lower “x” compositions. This small increase can possibly be linked to the presence of two bond lengths for the Be-Se bonds. One should also note that if the presence of Be chains and hence the two mode behavior was responsible for the observed increase in the value of σ^2, an increase in σ^2 should have been already observed for x = 0.27. This is however not the case, possibly due to the fact that at x = 0.27, there are only a few chains of Be in the sample thereby leading to a very small signal from the separate bond-lengths.

The anion (Se in our case) NNN bond shows two bond lengths corresponding to Se-Zn-Se and Se-Be-Se bonds. Fig. 1 also shows the variation of two bond lengths namely: Se-Zn-Se (R_{Se-Zn-Se}) and Se-Be-Se (R_{Se-Be-Se}) as a function of “x”. Like in the NN case, we find that the variation in the R_{Se-Be-Se} as a function of “x” is little over a factor of two less than R_{Se-Zn-Se} indicating the strong role of individual bond stiffness in determining the characteristics of the mixed crystals at least up to the second nearest neighbor. The NNN distances were evaluated from the Zn K edge data and are also shown in fig.1. We find that the Zn-Be composite lattice corresponds to a bond length close to the value predicted by VCA for different values of “x”.

Figure 2. The Debye-Waller factor for the nearest and next nearest neighbor distances as a function of “x”.

Figure 3. The bond angle evaluated from the nearest and next nearest neighbor distances.

Figure 4. NNN Se-Be-Se configuration with two adjacent tetrahedron.
To explain our observations of the NN distances, we have used the model proposed by Balzarotti et al. [5,10]. We have used this model to fit the experimentally determined nearest neighbor bond lengths. We find that the Be-Se and Zn-Se bond lengths calculated from the model are close to our experimental observations, indicating a random distribution of Be and Zn atoms in the mixed crystal.

The evaluated bond angles are shown in fig 3. The NNN distances R_{Se-Zn-Se} and R_{Se-Be-Se} can be evaluated by placing two tetrahedra next to each other as shown in fig. 4. Depending the types of the tetrahedron and their orientations, there would be different Se-Se distances across the Be atoms and the EXAFS measurement averages these distances (fig 4a and b: shows smaller and larger than undistorted NNN lengths respectively). Such an average over different possible Se-Se distances would lead to a large σ2 compared to the NN bond (fig 2). The bond angles Se-Zn-Se and Se-Be-Se are nearly the same throughout the range of “x” and very close to the ideal tetrahedron value of 109.8° because the bond lengths determined from EXAFS is an average over different values (both larger and smaller than the ideal tetrahedron values) and hence the bond angles are also an average. A reduction in the Zn-Se-Zn bond angle with increasing “x” (fig 3) is due to the fact that with increasing “x”, the probability of two and three Be atoms around Se atom increases. This pulls the Se atom towards the Be atoms, thereby decreasing the Zn-Se-Zn bond angle.

4. Conclusion:
To conclude, we have made a NN and NNN study of Zn_{1-x}Be_{x}Se mixed crystals for different values of “x”. The effects of percolating chains (expected to be observed in the form of a two-mode behavior in the Be-Se bond lengths) is observed as an increase in the σ2 value of the Be-Se bond at x = 0.42 and 0.55 as compared to smaller “x” values of 0.06, 0.16 and 0.27. This increase is consistent with the presence of two different bond lengths for the Be-Se bond lengths. The quantitative differences in the EXAFS data of this material system and other previously studied ternary systems has also been examined in detail in this work. These differences are attributed to the large contrast in the mechanical properties of the Be-Se and the Zn-Se bonds. Using a simple model of distorted tetrahedral we have also explained the observed variations in the various bond angles as a function of “x”.

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[11] There is an error in the formula for y2 in eq.5 in the work of A. Balzarotti et.al. The correct formula should read: y_2 = (a^2/4 + z_2^2 - a(z_2^2 - a^2/8 )^{1/2} )^{1/2}.

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