



Effect Of Substitution Of Anionic Metalloids In The Narrow Band Gap Semiconductor FeSb₂

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Abstract

We have investigated the structural and ⁵⁷Fe Mössbauer studies on two ternary anionically substituted (3.33 atom %) compounds Fe(Sb_{2-y}X_y) for (a) X = S, Se and Te (group VI elements) and also (b) As (group V element) in FeSb₂. Our aim is to see the effect of this anionic substitution in terms of the modifications occurring in the structural, electronic and magnetic properties of these ternary derivatives as compared to pristine narrow band gap semiconductor FeSb₂. As this anionic substitution directly replaces the antimony atom by either S or Se or Te or As atom in the first coordination sphere of the iron octahedra, it should change anisotropic electronic and magnetic properties and therefore it would be of interest. We would like to explore the magnetic ordering due to such anionic substitution as already been observed by Y.K. Sharma and F.E. Wagner for tellurium substituted FeSb₂, i.e. FeSb_{2-x}Te_x that compositions with 0 < x < 0.8 are ordered magnetically below 70K.

Keywords: Mössbauer Spectroscopy, FeSb₂, X-ray diffraction, Paramagnetism, Orthorhombic structure

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Introduction

Binary FeSb₂ crystallize in C18 marcasite type orthorhombic structure [1]. Petrovic et. al has observed very large magnetoresistance for FeSb₂ similar to the known GMR material (e.g., LaMnO₃) [2] and a temperature-induced spin state transition within a Fe t_{2g} multiplet was reported by measuring the thermal expansion and heat capacity [3]. We have observed a substantial change in the magnetic properties of FeSb₂ both by substituting cationically by Cr [4], Mn [5] and also anionically by Te [6]. Gonçalves da Silva predicted that FeSb₂ might be pushed over into a magnetic state by adding either a donor or an acceptor impurity [7].

⁵⁷Fe Mössbauer studies at 300K had been carried out by Y.K. Sharma et al. [6, 8] who concluded marcasite–arsenopyrite–marcasite type structural transition on the basis of quadrupole splitting variation with tellurium substitution for antimony into FeSb_{2-x}Te_x system. This result is in conformity with the earlier finding by Yamaguchi et al. [9] that the compositions between FeSb_{1.6}Te_{0.6} and FeSb_{0.6}Te_{1.4} are arsenopyrite type pseudo-orthorhombic or monoclinic whereas all other composi-

tion towards the end members are marcasite type orthorhombic structure.

We therefore here describe our efforts to synthesize and characterize anionically substituted FeSb₂ systems viz. with 3.33 atom % S, Se, Te and As substitution for Sb into FeSb₂.

Experimental Details

Synthesis

High purity (> 99.999%) element iron (Fe), antimony (Sb) and sulfur (S) or Arsenic (As) or selenium (Se) or tellurium (Te) were weighed and mixed in stoichiometric proportion and sealed under vacuum ($\approx 10^{-2}$ Torr) in a quartz ampoule. The ampoules were kept in a Kanthal wire wound furnace; initially the temperature was slowly raised from 300K to 1273K in the interval of 10 hrs to ensure the solid state diffusion of chalcogen or As and antimony with iron. Then the temperature was fixed at 1273K for 30hrs., in order to facilitate the complete mixing upon melting and then subsequently ampoules were quenched in to ice water. The furnace temperature was controlled by a temperature controller with an accuracy of

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about ± 10 K. The obtained black ingots were crushed in to fine powder and again put in to an evacuated ampoule for annealing.

All samples were annealed at 873K for about 15 days and finally quenched in to ice water. The second step of annealing process was repeated until the product was homogeneous. The annealed ingots were crushed in to a fine powder in an agate mortar and pastel in methanol and were dried at 350K. Using this procedure four compositions FeSb_{1.9}S_{0.1}, FeSb_{1.9}As_{0.1}, FeSb_{1.9}Se_{0.1} and FeSb_{1.9}Te_{0.1} were synthesized.

X-ray diffraction measurements

X-ray powder diffraction pattern was recorded at 300K for each specimen using a Philips 1840 model diffractometer operated at 30 kV and 30 mA by varying the 2θ angles in the step of 0.02° from 10° to 90° . The XRD data were analyzed using a standard program called "Powder X" which could index satisfactorily all the intense peaks.

⁵⁷Fe Mössbauer measurements

⁵⁷Fe Mössbauer measurements at 80K and 300K were performed using a 10 mCi ⁵⁷Co(Rh) source moving in constant acceleration mode.

The data were collected on to an MCD / PC using 512 channels. The Mössbauer spectra corresponding to the alloy specimens were calibrated using natural iron foil. The absorbers were prepared typically using 3 mg/cm² of natural iron content for these specimens which corresponds to 50 mg/cm² of the specimen. The relative absorption in Mössbauer spectra observed varied from 4.42 % to 6.80 % for these specimens.

⁵⁷Fe Mössbauer measurements at 80K were performed in a variable temperature cryostat with the source at room temperature. The temperature was controlled within ± 0.01 K range for these measurements. The absorber

(sample) was sandwiched in between two aluminium foils to achieve a good thermal equilibrium. The Mössbauer spectra of all specimens were fitted using a standard data analysis program developed by Jernberg and Sundqvist.

Results and discussion

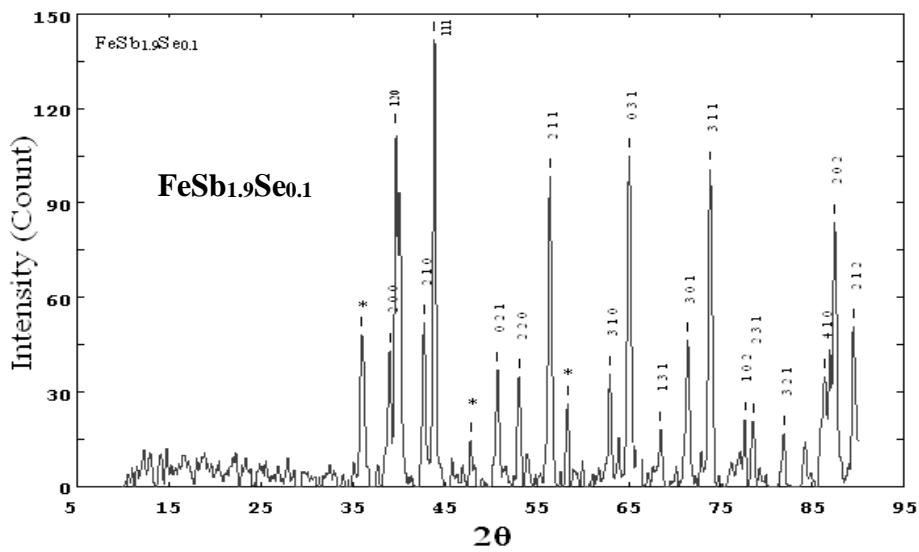
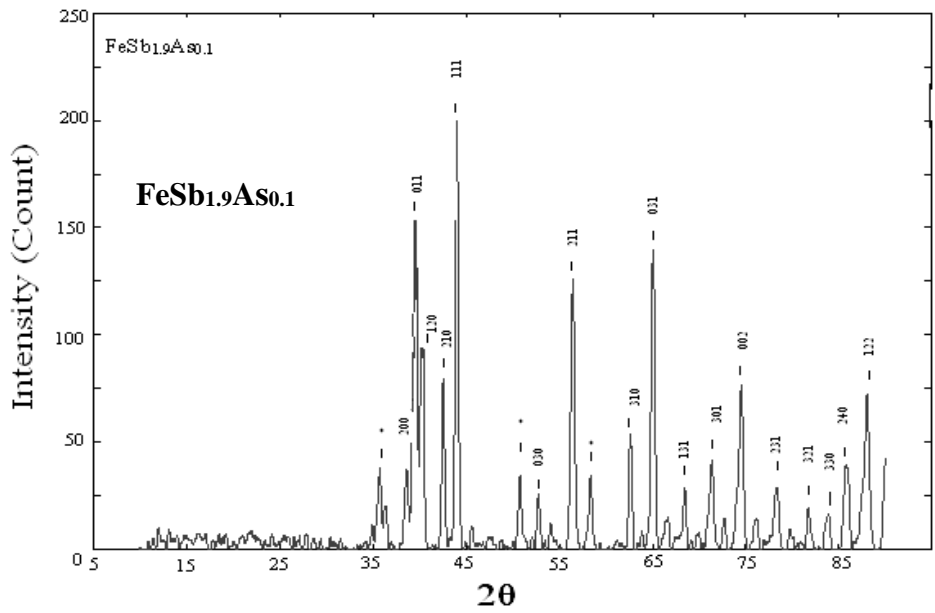
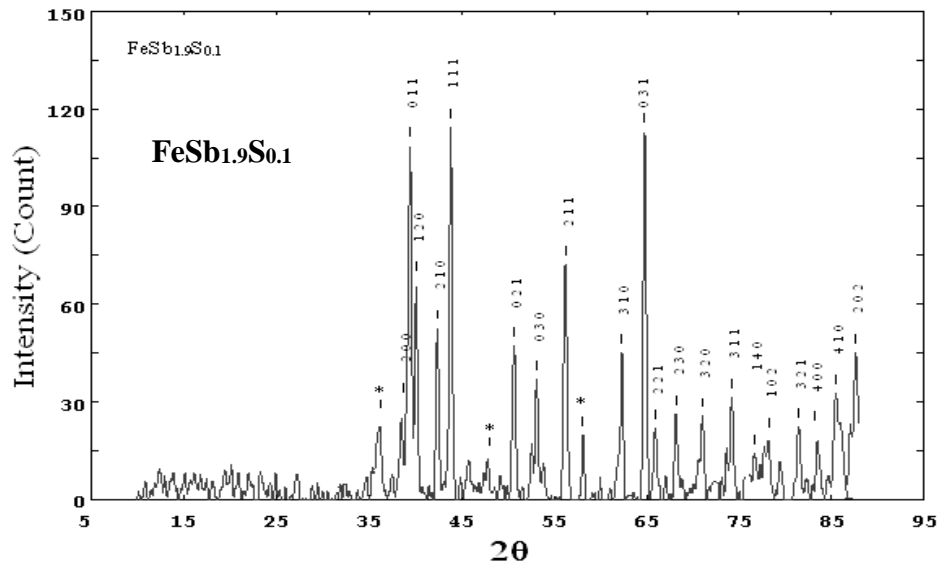
X-ray diffraction analysis

Fig.1 shows the XRD patterns for all four specimens, which were indexed and analyzed using "Powder X" indexing program [10]. The experimental peaks, and (hkl) indexing, have been shown in this figure.

For all the series specimens, the large intensity peaks observed corresponds to the reflections (011), (111), (211), (031) and (122). Indexed and unindexed reflections found through "Powder X" indexing program [10]. The asterisked peaks correspond to FeK _{β} radiation.

There is neither any intense peak corresponding to an elemental impurity of Fe or Sb or other elements like S, As, Se, Te or their binary phases e.g. FeSb₂, etc. observed in the patterns of the series specimens. Table 1 shows the lattice parameters (a, b, c) and unit cell volume (V) for all four compositions. Fig 2 displays the lattice parameters (a, b, c) and unit cell volume (V) plotted against the atomic number of substituted anions. It reveals the increase in the lattice parameters and unit cell volume upon anionic substitution of elements from S to Te. There is a variation of 2 % in unit cell volume on going from S to Te substitution for Sb in FeSb₂. The lattice parameters for FeSb₂ match well with those reported earlier by Petrovic et al. [11]. The unit cell volume for FeSb_{1.9}S_{0.1}, FeSb_{1.9}As_{0.1} and FeSb_{1.9}Se_{0.1} is less than that for FeSb₂ while for FeSb_{1.9}Te_{0.1} it is higher than FeSb₂. These results may be attributed to the increasing substituent atom size (of the anionic atom) as one goes from S to Te.





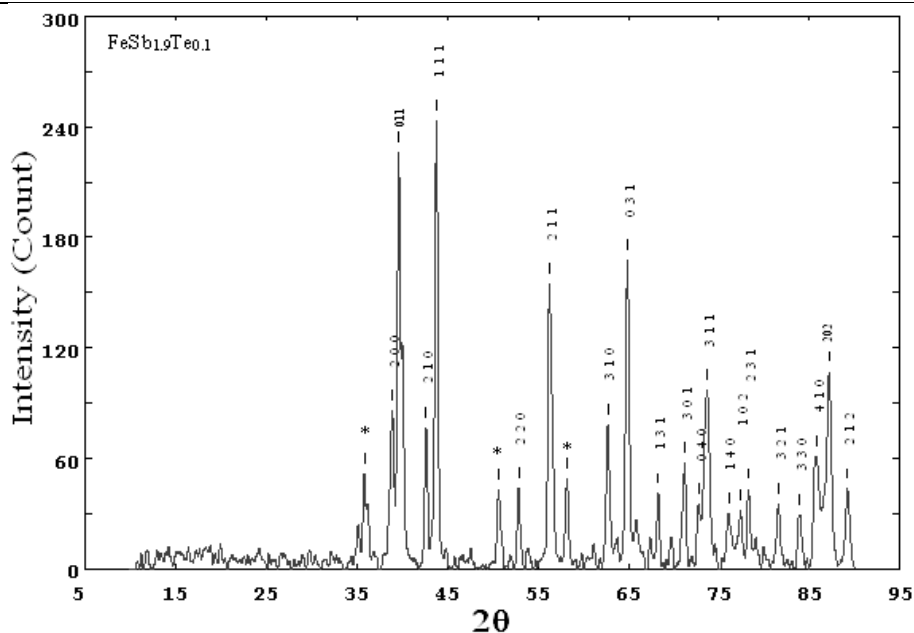


Fig.1XRD patterns for FeSb_{1.9}S_{0.1}, FeSb_{1.9}As_{0.1}, FeSb_{1.9}Se_{0.1}& FeSb_{1.9}Te_{0.1} at 300K.

Table 1 Lattice parameters and unit cell volume for Fe(Sb_{2-y}X_y) at 300K.

S.No.	Specimen	a(A ⁰)	b (A ⁰)	c(A ⁰)	V (A ⁰) ³
1	FeSb _{1.9} S _{0.1}	5.825	6.490	3.193	120.709
2	FeSb _{1.9} As _{0.1}	5.827	6.515	3.201	121.519
3	FeSb _{1.9} Se _{0.1}	5.837	6.519	3.207	122.030
4	FeSb _{1.9} Sb _{0.1}	5.840	6.540	3.203	122.334
5	FeSb _{1.9} Te _{0.1}	5.840	6.535	3.224	123.042

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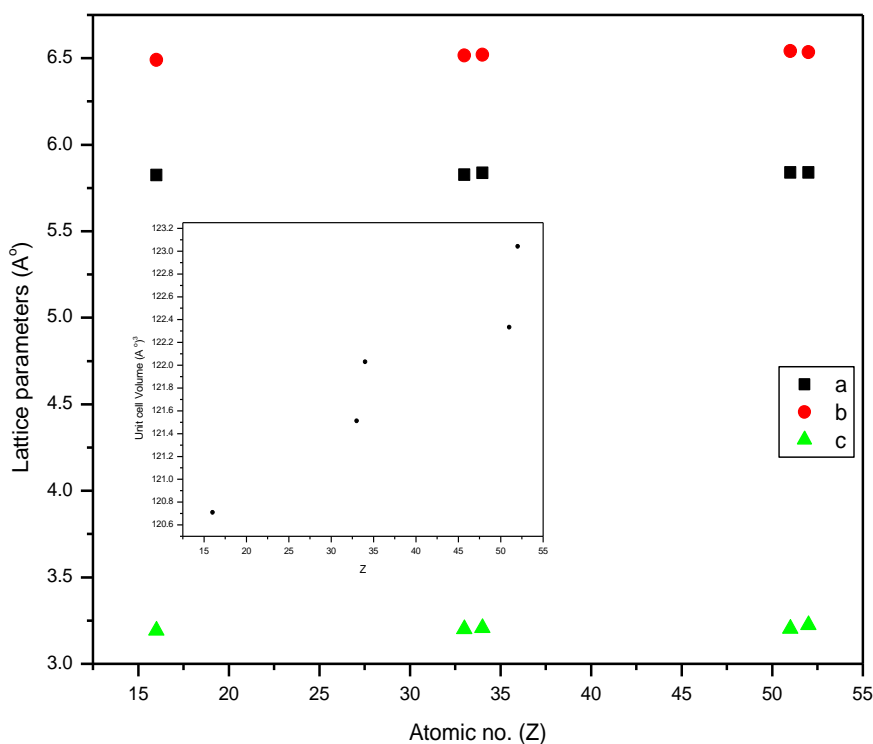


Fig. 2Lattice parameters versus atomic no. Z (substituted anions) in FeSb₂ (inset shows unit cell volume vs. Z)



⁵⁷Fe Mössbauer measurements

Spectra at 300K

Fig.3 shows the ⁵⁷Fe Mössbauer spectra at 300K for the specimens FeSb_{1.9}S_{0.1}, FeSb_{1.9}As_{0.1}, FeSb_{1.9}Se_{0.1} and FeSb_{1.9}Te_{0.1} respectively. The experimental data points have been shown by dots where as the solid line is the computed envelope of the single quadrupole split doublet.

Table 2 gives the values of Mössbauer parameters viz. Isomer shift (IS), Quadrupole splitting (QS), Line width (LW) and χ^2 , the goodness-of-fit parameter. Each spectrum was fitted with an acceptable χ^2 . The line width of the specimens ranges between 0.28 - 0.30 mm/s, which is comparable with the width for standard natural iron absorber at 300K. The ⁵⁷Fe Mössbauer spectra for all specimens therefore indicate paramagnetic character at 300K.

Isomer Shift (IS)

It may be seen from table 2 that IS values do not exhibit much change from S to Te substitution for Sb into FeSb₂ and are indicative of iron staying in the low spin state with highly covalent Fe-Sb(X) bonds in all these compositions as in the case of FeSb₂. This fact is in accordance with the earlier findings of Temperley et al. [12]. The constancy of isomer shift around the value 0.45 mm/s (with respect to iron metal) for these series compositions may be explained qualitatively as follows:

The isomer shift is mainly measure of s-electron density at the nucleus of the Mössbauer atom (Fe atom at present). This s-electron density is mainly contributed from two factors; one is from filled s-orbitals in inner electron shells and another from partially filled outer most orbitals (valence orbitals) where the Mössbauer atom's own valence electrons as well as electrons from surrounding ligands are accommodated constituting the chemical bond. This valence electron contribution is very much sensitive to changes in electronic configuration of valence shell. This valence electron population is subject to change by substituting the chalcogen atom (e.g. S, Se, Te) or a

pnictogen atom (e.g. P, As etc.) for antimony as it will be replaced in the iron octahedral surrounding in the first coordination sphere and due to electronegativity difference it will also affect Sb-Fe-X type covalent bonds.

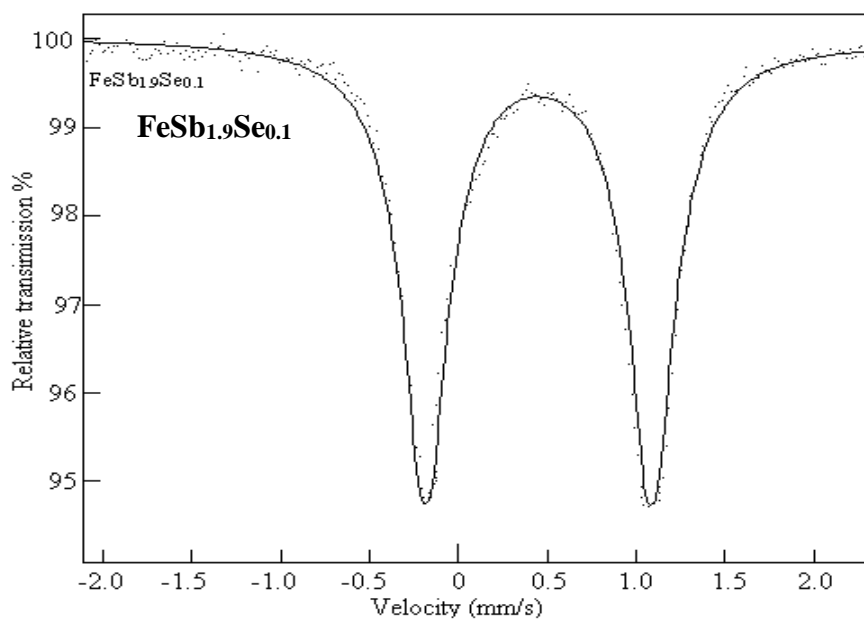
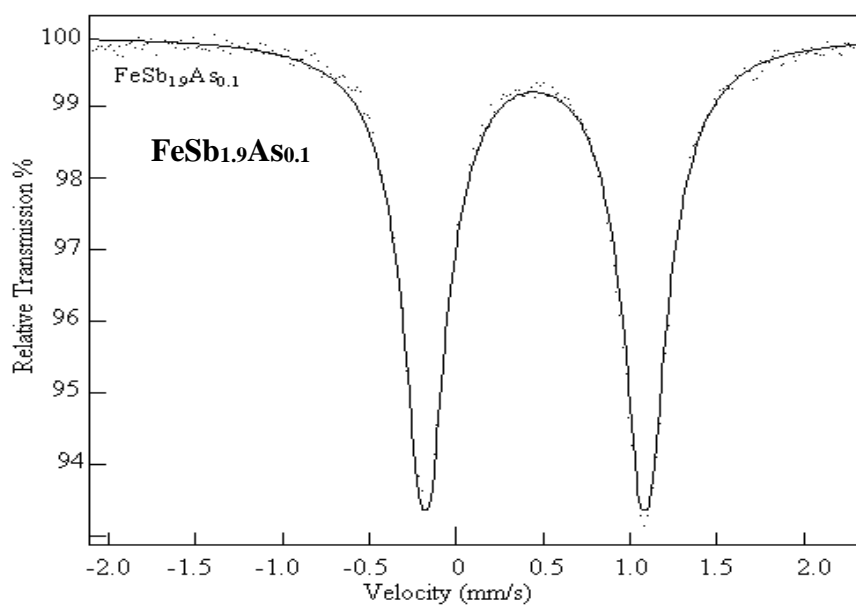
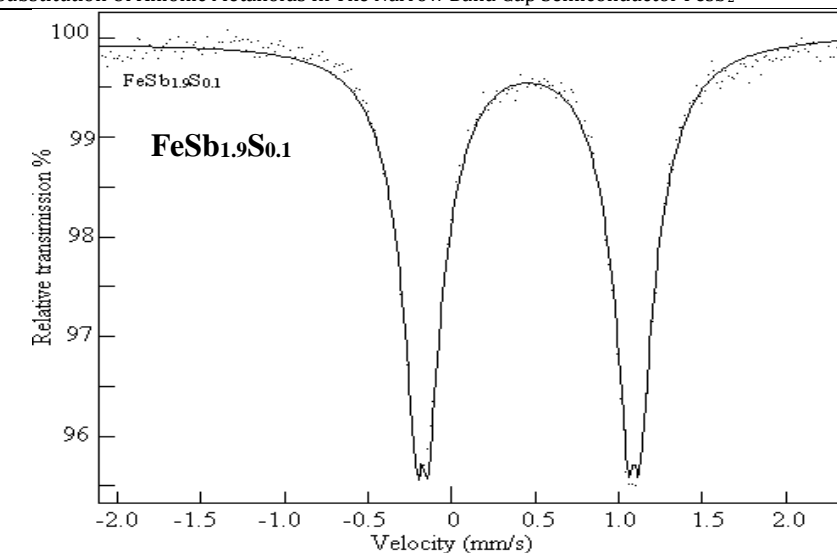
It has been shown that the order of increasing electronegativity of the ligands is S < As < Se < Te (Pauling 1960 [3]) which has clearly been exhibited by the increasing IS values for the compounds FeS₂, FeSe₂ and FeTe₂ [13]- all orthorhombic structured marcasites similar to the ones we have synthesized by substituting S or Se or Te or As for Sb into FeSb₂. However, since we have substituted only 3.33 atom% of these chalcogen or pnictogen atom, the number of Sb-Fe-X bonds compared to Sb-Fe-Sb bonds will not be significant and hence one may expect the constancy of IS values. We would like to add that due to low spin state as well there may not be a significant change in IS values while substituting the anions as also was observed by Y.K. Sharma et al. [6] for Fe(Sb_{1-x}Te_x)₂ series compositions through ⁵⁷Fe Mössbauer studies at 300 K.

Quadrupole splitting (QS)

The QS values exhibit a small increase in going from S to Te substituted FeSb₂ compositions of the series. One may understand this change in QS as: The QS is a measure of the asymmetry of the total electronic wave function (or EFG) at the Fe nucleus which could be due to two factors. One of these is from the valence electron contribution and the other from the lattice. Due to increase in unit cell volume of about 2 %, on going from S to Te substitution for Sb, the lattice contribution to the QS may also be expected to increase.

As anionic substitution may be expected to affect the covalent character of Sb-Fe-X type bonding which in turn will affect the degree of distortion of the iron octahedral coordination. This should increase the lattice contribution to the QS. Hence, the net QS value may increase on going from S to Te substitution for Sb for the series specimens.





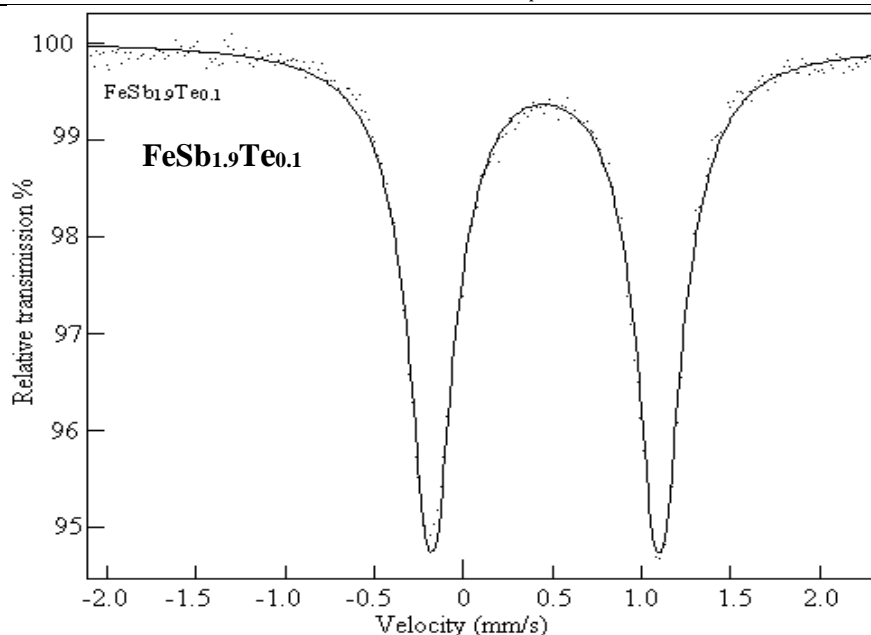


Fig. 3 ⁵⁷Fe Mössbauer spectra for Fe(Sb_{2-y}X_y) (X = S, As, Se & Te) System at 300K.

Table 2 ⁵⁷Fe Mössbauer parameters at 300 K for system for Fe(Sb_{2-y}X_y) for X = S, As, Se & Te, Isomer shift δ is given with respect to α - Fe.

S.No.	Specimen	IS (δ) (mm/sec)	QS (Δ) (mm/sec)	LW(Γ) (mm/sec)	χ^2
1	FeSb _{1.9} S _{0.1}	0.455 (± 0.0006)	1.266 (± 0.001)	0.280 (± 0.002)	2.011
2	FeSb _{1.9} As _{0.1}	0.450 (± 0.0004)	1.269 (± 0.0008)	0.304 (± 0.001)	3.010
3	FeSb _{1.9} Se _{0.1}	0.447 (± 0.0005)	1.272 (± 0.001)	0.308 (± 0.001)	3.206
4	FeSb _{1.9} Sb _{0.1} (FeSb ₂)	0.452 (± 0.0003)	1.273 (± 0.0006)	0.294 (± 0.0005)	3.208
5	FeSb _{1.9} Te _{0.1}	0.456 (± 0.0005)	1.280 (± 0.001)	0.308 (± 0.001)	2.270

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Conclusions

On the basis of the experimental data we conclude that

- The XRD analysis suggests the single phase orthorhombic crystal structure at 300K for FeSb_{1.9}S_{0.1}, FeSb_{1.9}Se_{0.1}, FeSb_{1.9}As_{0.1} and FeSb_{1.9}Te_{0.1} and therefore here exist solid solubility of S, Se, Te and As into FeSb₂ upto 3.33 atom% of these atoms. The lattice parameters and unit cell volume increases from S to Te substitution.
- ⁵⁷Fe Mössbauer spectra for all specimens indicate the paramagnetic character at 300K.

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