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Received 24 May
and accepted 25 June 1976

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Association of iron microtraces with oxygen in tin chalcogenides

A factor which affects the stabilization of the properties of thermoelectric materials of IV–VI semiconductors and the service life of thermoelectric generators is the diffusion of impurities from bridging materials, such as Fe in thermoelements. In addition to this, processes may occur between these doping elements and impurities which are inevitably present in the matrix. All these factors complicate considerably the picture of degradation of materials. In this work we demonstrate, by means of Mössbauer effect measurements, that in the IV–VI semiconductor subgroup of tin chacogenides, one of which (SnTe) is used at the bridge-thermoelement interface, an association exists between iron and oxygen successively diffused in the matrix. Moreover, in the presence of traces of iron, the oxygen is not randomly distributed on the crystallographic sites.

Several studies of the ^{57}Fe stabilization forms in single lattices using the Mössbauer effect have been reported [1–5]. In some instances more than one state of charge has been identified and models for the stabilization form have been proposed. Fano and Ortalli [5] have reported that for Sn chalcogenides doped with Fe, different peaks are seen in the presence of doping elements such as oxygen which partially substitute tellurium in the lattice. Thus it can be assumed that the cluster formed by ^{57}Fe in an interstitial position with its neighbours [$FeTe_4$], partially change into other forms such as:

$$[FeTe_4] \rightarrow [FeTe_xO_{1-x}] \qquad (1)$$

with $x = 1, 2 \ldots$, due to the oxidization effect.

In this work we attempt to ascertain if the existence of these clusters reflects a random distribution of oxygen in the various crystallographic sites of the single crystal, or if the substitution of oxygen for tellurium in the vicinity of the iron is due to the preference of the iron to associate itself with the oxygen.

To investigate this, measurements were made of the variation of the Mössbauer peak intensity corresponding to the various clusters with annealing time at 400° C in inert atmosphere. SnS and SnTe single crystals doped with microtraces of ^{57}Co were used and successively submitted to oxidation for 5 h at 400° C in an atmosphere of $\frac{1}{3}O_2$ and $\frac{2}{3}N_2$ were examined. The synthesis of the single crystals, the doping with ^{57}Co, the oxidation process and the measurement techniques are reported in [5], together with the typical spectrum of non-oxidized SnS(^{57}Fe) and SnTe(^{57}Fe) samples.

The homogeneous distribution of the transition elements in the samples was tested prior to oxidation, by comparing the spectrum intensity of that side of the sample side on which $^{57}CoCl_2$ was deposited with the spectrum intensity of the opposite side. ^{57}Co was considered to be homogeneously distributed throughout the sample when the two intensities were equal.

The spectrum of SnS(^{57}Fe) after the oxidation process is shown in Fig. 1a. The curve can be resolved into two quadrupole couplings (Q_1 and Q_2); Q_1 has the same Mössbauer parameters (δ, ΔE, *FWHM*) as the non-oxidized samples (see Table I). Any uncertainty in the computer fitting was removed using the folowing facts: (1) all spectra obtained for samples oxidized at

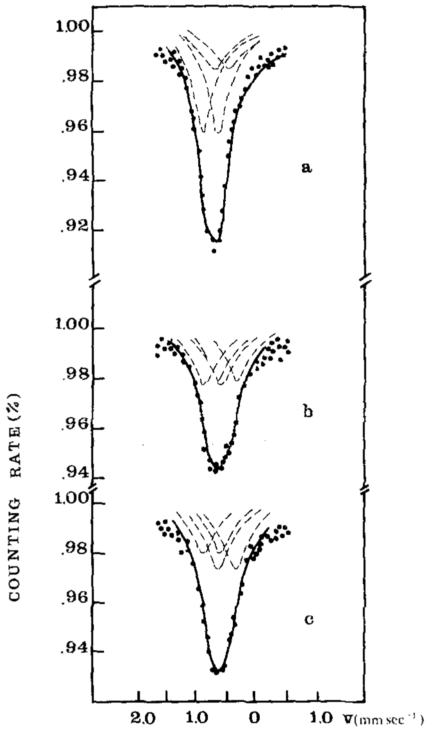

Figure 1 Absorption Mössbauer spectra of ^{57}Co diffused in SnS (a) after the oxidation process, (b) after 10 h annealing, (c) after 16 h annealing.

different annealing times show the same *FWHM* and baricenter shift which is inconsistent with a single quadrupole splitting. (2) These spectra (for oxidation time $\leqslant$ 5 h) can always be resolved into two doublets (Q_1 and Q_2) having the same value of δ, ΔE and *FWHM*. (3) The latter spectra after annealing in an inert atmosphere can again be resolved into two doublets with the Mössbauer values equal to those previously obtained, but with different intensities (see Table I). For longer oxidation times (7 to 8 h; above this there is a danger that the sample might shatter) the spectra become wider, the barycentre shifts and that part of the spectrum with the lower values of shift becomes smaller. It is therefore necessary to consider other hypotheses.

Values of Q_2 ($\delta = -0.47$ mm sec^{-1} $\Delta E = 0.25$ mm sec^{-1} $\Gamma_{1/2} = 0.52$ mm sec^{-1} can be ascribed to SnS(^{57}Fe) where oxygen is present in the neighbouring Fe. Fig. 1b shows a spectrum for the same sample as that used in Fig. 1a, but the sample was held at 400° C for 10 h in an inert atmosphere (pure H_2; the use of a reducing atmosphere of H_2 does not appear to influence the spectrum). It can be seen (Fig. 1b) that the spectrum is still resolved into two doublets having the same δ, ΔE and *FWHM* as that of Fig. 1a, but the intensity of Q_1 is notably reduced and the intensity of Q_2 is notably increased. Again after 6 h annealing at 400° C in an inert atmosphere, the intensity of Q_1 is further reduced while the intensity of Q_2 increases (Fig. 1c).

An exact comparative quantitative analysis cannot be made for Q_1 and Q_2 because $f(Q_1) \simeq f(Q_2)$ is very approximate, and under these experimental conditions, the possibility that with an increase of annealing time, diffusion of oxygen within the deepest area of the single crystal can provide a contribution to the $f(Q_2)$ cannot be excluded. Nevertheless it must be noted that the anionic part of the single crystal matrix, even after 4 h oxidation and 16 h annealing is made up of tellurium. In fact, X-ray analysis does not show any appreciable variation with respect to the non-oxidized samples, thus the oxygen content is less than a few precent. Therefore, the intensity of the peak ascribed to the iron surrounded by tellurium partially substituted with oxygen would have a

TABLE I Values of the relative intensity (*I*), isomer shift (δ), quadruple splitting (ΔE) and width at half-height (*FWHM*) for ^{57}Co diffused in SnS

		I(%) (±0.2)	δ(mm sec^{-1}) (±0.03)	ΔE(mm sec^{-1}) (±0.05)	*FWHM*(mm sec^{-1}) (±0.03)
After 5 h	Q_1	4.0	−0.70	0.25	0.47
oxidation	Q_2	1.5	−0.47	0.25	0.52
After 10 h	Q_1	2.2	−0.70	0.27	0.47
annealing	Q_2	2.0	−0.47	0.24	0.52
After 16 h	Q_1	2.0	−0.70	0.26	0.47
annealing	Q_2	2.7	−0.47	0.25	0.52

much lower peak intensity compared to the first peak $[f(Q_1) \gg f(Q_2)]$. The intensity of Q_2 is, however, higher than Q_1. Therefore, a random oxygen distribution can be excluded in the presence of microtraces of iron. The large amount of iron with the neighboring tellurium partially substituted by oxygen shows the existence of an association between interstitial iron and the substituted oxygen.

The spectrum of SnTe(^{57}Fe) oxidized for the same time is split as shown in Fig. 1a. The shift of the isomer shift of Q_2 and thus the variation of $|\psi(0)|^2$ has the same δ value as oxidized SnS(^{57}Fe) ($\delta \simeq 0.23\,\text{mm sec}^{-1} \simeq 1.15 \times 10^{-7}\,\text{eV}$). Annealing in an inert atmosphere also leads to an increase in the intensity of Q_2, which is comparable to that occurring in SnS(^{57}Fe). In all events, the appearance of more complex clusters is dependent upon a higher oxygen concentration in these materials.

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Received 12 July
and accepted 27 July 1976

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Dynamic K_{IC} and dynamic flexural strength in HS-130 Si_3N_4

The mode I fracture-toughness value, K_{IC}, of hot-pressed Si_3N_4 has been shown to increase significantly with increasing temperature above 1000° C [1, 2]. However, at normal testing speeds, this increase in K_{IC} is not associated with an increase in fracture strength, σ_f; rather σ_f decreases rapidly with increasing temperature above 1000° C [3, 4]. The increase in K_{IC} and the decrease in σ_f at high temperatures have been attributed to the presence of a glassy grain-boundary phase whose viscosity decreases with increasing temperature. At high temperatures fast fracture is preceded by considerable sub-critical crack growth due to grain-boundary sliding [4] which decreases σ_f. On the other hand, the low-viscosity glassy phase absorbs energy during fast fracture, causing an increase in K_{IC}. Under impact loading conditions (i.e. high loading rates), the dynamic K_{IC} and σ_f have not been determined. Since rapid loading conditions should minimize or eliminate slow crack growth, it was of interest to determine $K_{IC(\text{dynamic})}$ and to examine whether fracture strength is reduced at high temperatures. The $K_{IC(\text{dynamic})}$ was measured by employing a controlled surface-flaw technique [2] in conjunction with an instrumented drop-weight test apparatus [5].

A controlled, Knoop indentation flaw [2] was placed on the tensile side of each of six HS-130 (Norton Co, Worcester, Mass), hot-pressed Si_3N_4 bend bars, 6.35 mm × 3.17 mm × 50 mm long. An indentation load of 2.6 kg was applied, producing a nearly semicircular, sharp microcrack having ~ 0.07 mm depth and 0.170 mm surface length. The bend bars were then annealed at 1300° C for 1 h in air to relieve the residual stress around the indent [2, 6]. Two bars were broken in four-point bending at room temperature at a cross-head speed of 0.005 cm min^{-1}, and $K_{IC(\text{static})}$ was determined from the fracture stress and flaw dimensions. The remaining bars were broken in three-point bending in an instrumented drop-weight test apparatus used for impact testing [5]. In this apparatus the bar deflects into a laser beam, and the change in beam intensity is recorded photographically as a function of time for measurement of the deflection at fracture. Standard elastic analysis of the bending of bars [7] was then used to compute the fracture strength from the measured values of deflection. A 1.27 cm diameter steel ball was used as the impactor, and a deflection rate of 1.3×10^4 cm min^{-1} was measured at fracture. Two bars were fractured at room temperature and two at 1300° C. The flaw dimensions were measured from the fracture surfaces and, using fracture-mechanics analysis, $K_{IC(\text{dynamic})}$ was calculated from values of σ_f