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Crystal structure and Raman scattering characterization of Cu₂Fe₁₋ _xCo_xSnS₄ chalcogenide compounds



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ABSTRACT

This work reports the synthesis by solid–state reaction of $Cu_2Fe_{1-x}Co_xSnS_4$ solid solutions. Crystal structures of $Cu_2Fe_{0.8}Co_{0.2}SnS_4$ and $Cu_2Fe_{0.6}Co_{0.4}SnS_4$ were investigated by single crystal X-ray diffraction. Both phases crystallize in the tetragonal stannite-type structure. The volume of the tetrahedral [MS₄] (M = Fe, Co) presented the highest distortion, with Edge-Length Distortion (ELD) indices ~2% from the ideal tetrahedron. The powder X-ray diffraction (XRD) patterns of $Cu_2Fe_{1-x}Co_xSnS_4$ (x = 0.2, 0.4, 0.6 and 0.8) has been refined by Rietveld method. No secondary phases were detected in XRD patterns. An analysis of the vibrational properties of $Cu_2Fe_{1-x}Co_xSnS_4$ was performed using Raman scattering measurements. The Raman peaks were analyzed by fitting of the spectra and subsequently identifying the vibrational modes by comparison with experimental and theoretical data from Cu_2FeSnS_4 (CFTS) and Cu_2CoSnS_4 (CCTS) end-members. The spectra from $Cu_2Fe_{1-x}Co_xSnS_4$ show that there is a variation in the frequency of the main A_1 peak at ~320 cm⁻¹ together with a decrease in the secondary mode intensity at ~285 cm⁻¹. Full Width at Half Maximum (FWHM) and the intensity of the Raman peaks were confirmed by temperature-dependent magnetization measurements performed in the antiferromagnetic $Cu_2Fe_{1-x}Co_xSnS_4$ solid solutions.

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1. Introduction

The need to satisfy the demand for green energy on our planet has encouraged the development of new methods for generating energy. One of the main solutions to this problem is to take advantage of solar energy. The development of more efficient and low-cost solar cells is one of the main objectives in the research of new materials. The quaternary semiconductor copper-zinc-tinsulfur Cu₂ZnSnS₄ (CZTS), copper-iron-tin-sulfur Cu₂FeSnS₄ (CFTS) and their corresponding solid solutions have become the focus of interest due to their application as new absorbent materials for solar cells and their interesting properties, namely high absorption coefficients (>10⁻⁴), optimum band gaps and high power energy conversion rates of 12.6% [1,4]. In addition, they have economic and ecological advantages because they are formed by elements that are abundant, cheap and of low toxicity in comparison with other types

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of absorbents such as Cu(In, Ga) (S, Se)₂ (CIGS) [1,2].

It is known that the CFTS compound has a stannite-type crystal structure (space group $I\overline{4}2m$), while CZTS crystallizes in a kesterite structure (space group $I\overline{4}$). Both are tetragonal structures consisting a *ccp* array of sulfur anions, with metal cations occupying one half of the tetrahedral voids. These are closely related with reduction of symmetry characterized by an increase in the degree of freedom in the crystallographic positions of the sulfide anion from the (1/4,1)4,1/4) in the stannite-type to the (x,y,z) in the kesterite structure. Their different crystal symmetry is due to the different distribution of metal cations at their tetrahedral sites. Besides, the binding energy difference between the stannite and kesterite structures is small (approximately 3 meV/atom), it is suggested that both structures may coexist in the samples [2,3]. Since the multinary solid solutions Cu₂(M'M")SnS₄ can crystallize in either type of structure, the study of these structures by single-crystal x-ray diffraction is of interest. The structures of stannite and kesterite only differ in their distribution of the metal cations, so they are very difficult to differentiate using powder X-ray diffraction (XRD) patterns. However, the eventual existence of structural or phase inhomogeneities in the absorbers also needs to be clarified,



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Table 1
Crystallographic data and structure refinement details.

Compound	Cu ₂ Fe _{0.8} Co _{0.2} SnS ₄	Cu ₂ Fe _{0.6} Co _{0.4} SnS ₄
Crystal size (mm ³)	0.1 imes 0.05 imes 0.04	0.10 imes 0.07 imes 0.08
Crystal color	Black	Black
Crystal system	Tetragonal	Tetragonal
Space group, Z	I42m,2	$I\overline{4}2m, 2$
Lattice constants (Å)	a = 5.4190(8)	a = 5.4110(8)
	c = 10.843(2)	c = 10.853(2)
Cell volume (Å ³)	318.41(9)	317.76(9)
Temperature (K)	150(2)	150(2)
Wavelength, Mo Ka	0.71073	0.71073
Equipment	KappaCCD	KappaCCD
Absorption coefficient (mm^{-1})	14.037	15.164
θ-range (°)	$3.76 < \theta < 27.40$	$3.75 < \theta < 27.44$
hkl-range	$-7 \le h \le 6$	$-7 \le h \le 6$
	$-7 \leq k \leq 7$	$-7 \le k \le 6$
	$-14 \le l \le 13$	$-14 \le l \le 14$
No. of reflections, $R_{int.}$, R_{σ}	2292, 0.03251, 0.0160	1424, 0.0254, 0.0212
No. of independent reflections	212	211
No. of parameters	14	14
Flack parameter	0.01(12)	0.05(10)
Extinction coefficient	0.032(3)	0.0114(4)
$R (I > 2\sigma_{I}), R (all reflections)$	0.0276, 0.0276	0.0272, 0.0272
$wR2 (I > 2\sigma_1), wR2$ (all reflections)	0.0823, 0.0823	0.0867, 0.0867
Goodness-of-Fit ($GooF = S$)	1.339	1.350
Largest difference peaks	1.922, -0.836	1.791, -0.911

particularly because of possible impact on the characteristics of the solar cells. In this respect, Raman scattering can provide more reliable information about the crystalline structure of the samples as well as on the possible presence of structural and chemical inhomogeneities as secondary phases or polytypes.

We have previously reported on the crystal structure and magnetic properties of the Cu₂Mn_{1-x}Co_xSnS₄ with kesterite structures, whereas both Cu₂MnSnS₄ (CMTS) and Cu₂CoSnS₄ (CCTS) endmembers crystallize in a stannite-type structure [4]. Additionally, we have reported on the synthesis, structural characterization and magnetic properties of Cu₂Mn_xFe_{1-x}SnS₄ solid solutions [5]. In this work, we report the synthesis, crystallographic characterization, magnetic properties and vibrational analysis of new Cu₂Fe_{1-x}Co_xSnS₄ solid solutions obtained by isomorphic substitution of Fe²⁺ cation fractions with paramagnetic Co²⁺ cations. The aim of this work is to study the influence of x values on their physical properties. In addition, this paper presents a detailed spectroscopic analysis of these phases, which was performed using Raman scattering measurements.

2. Experimental details

2.1. Synthesis

Polycrystalline Cu₂Fe_{1-x}Co_xSnS₄ compounds were prepared by

 Table 2

 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$).

directly combining high-purity element powders (99.99%, Aldrich) in stoichiometric amounts. All manipulations were carried out under an argon atmosphere. The reaction mixtures were sealed in evacuated quartz ampoules and placed in a programmable furnace where they were first slowly heated from room temperature to 850 °C and then held at this temperature for 72 h. Immediately thereafter the ampoules were quenched in liquid nitrogen.

2.2. Structure determination

Single crystals of two reaction products (x = 0.2 and 0.6) were isolated. X-ray diffraction data were collected at room temperature on a Bruker Kappa CCD diffractometer, using the graphitemonochromatized MoK α_1 radiation ($\lambda = 0.71073$ Å). The collection of intensity data was carried out with the program COLLECT [6]. Cell refinement and data reduction were carried out with Dirax/lsq and EvalCCD programs [7,8]. The collection of intensity data was carried out with the program SMART [9]. Cell refinement and data reduction were carried out with the program SAINT [20]. Multi-scan absorption correction was performed with SADABS program [10]. Cu₂Fe_{0.8}Co_{0.2}SnS₄ and Cu₂Fe_{0.6}Co_{0.4}SnS₄ were refined in *I*42*m* (no.121) space group, where the Cu cations are located in the 4d position, while Co/Fe, Sn, and the S anions are at positions 2a, 2b, and 8i respectively. The crystal structures were refined in full-matrix least-squares using the SHELXL package of crystallographic

Atom	Wyckoff multiplicity	Occupancy	х	У	Z	Ueq ^a
Cu ₂ Fe _{0.8} Co _{0.2} Si	nS ₄					
Cu	4d	1	1/2	0	3/4	0.0188(5)
Fe/Co	2a	0.8/0.2	0	0	1	0.0108(5)
Sn	2b	1	1/2	1/2	1	0.0128(5)
S	8i	1	0.2431(3)	0.2431(3)	0.87109(15)	0.0109(6)
Cu ₂ Fe _{0.6} Co _{0.4} Si	nS ₄					
Cu	4d	1	1/2	0	3/4	0.0196(5)
Fe/Co	2a	0.6/0.4	0	0	1	0.0116(5)
Sn	2b	1	1/2	1/2	1	0.0143(5)
S	8i	1	0.12905(19)	0.12905(19)	0.7571(3)	0.0117(5)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Edge	length	distortion	S-S	(ELD) and	tetrahedral	angle	variance	(TAV)	۱.
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Tetrahedral	ELD ^a (%)	TAV ^b (°)
Cu ₂ Fe _{0.8} Co _{0.2} SnS ₄		
CuS ₄	0.7	1.6
MS ₄	1.5	7.4
SnS4	0.2	0.06
Cu ₂ Fe _{0.6} Co _{0.4} SnS ₄		
CuS ₄	1.1	1.7
MS ₄	1.4	6.2
SnS ₄	0.1	0.05

^a EDL = $\frac{100}{6} \sum_{i=1}^{6} \frac{(S-S)_i - (\langle S-S \rangle)}{\langle S-S \rangle}$

^b $TAV = \frac{100}{6} \sum_{i=1}^{6} \frac{(\theta_i - 109.4712)^2}{5}$, where θ_i are the angles of the S-Metal-S bonds in the tetrahedra and $\langle S-S \rangle$ is the average sulfur–sulfur distance in the tetrahedral edge.

programs [11]. Software used to prepare material for publication was PLATON [12]. The refined occupation factors of Fe and Co cations were consistent with the X-Ray energy-dispersive spectroscopy (EDS) analysis averaged over several areas of the single-crystals used in the diffraction experiments. Moreover, Fe and Co atoms (same crystallographic site) were constrained to have identical thermal parameters. Detailed crystallographic data and refinement results are summarized in Table 1. The atomic coordinates, equivalent isotropic thermal parameters, selected bond distances and angles are listed in Tables 2 and 3. The CIF files were deposited in the FIZ Karlsruhe database (76344 Eggenstein-Leopoldshafen, Germany; email: crysdata@fiz-karlsruhe.de; fax: (49)7247–808–666). The depository numbers are CSD-429465 for Cu₂Fe_{0.8}Co_{0.2}SnS₄ and CSD-429466 for Cu₂Fe_{0.60}Co_{0.40}SnS₄.

2.3. Powder X-ray diffraction measurements

Powder X-ray diffraction patterns were collected at room temperature on Bruker D8 Advanced diffractometer, with CuK_{α} radiation ($\lambda = 1.5406$ Å) in the range 5° < 2 θ < 80°. XRD patterns were refined by Rietveld method using the MAUD software [13]. Standard LaB₆ sample was used for measuring the instrumental profile.

2.4. SEM-EDS analysis

The chemical compositions of the samples were determined by energy-dispersive X-ray analysis (SEM-EDS) using a JEOL 5400 system equipped with an Oxford LinK ISIS microanalyzer. The working distance was 35 mm and the accelerating voltage was set to 22.5 kV. Samples were mounted onto double-sided carbon tape, which was adhered to an aluminum specimen holder. EDS data were collected for 60 s.



Fig. 1. Unit cell of the $Cu_2Fe_{1-x}Co_xSnS_4$ structure viewed along [010] (left) and [100] (right) showing the tetrahedra [SnS₄], [CuS₄], [MS₄] (M = Fe, Co) with Sulfur atoms in the corners.

2.5. Magnetic measurement

Magnetic measurements were performed on pelletized powder samples using a Quantum Design MPMS XL5 SQUID magnetometer between 2 and 400 K, under different applied fields 500 Oe for zero-field-cooled/field-cooled (ZFC/FC) cycles. The effective paramagnetic moments were evaluated from susceptibility measurements at high temperatures and high applied fields ($H_{app} = 10$ kOe).

2.6. Raman spectroscopy

The Raman spectra of Cu₂FeSnS₄, Cu₂Fe_{0.8}Co_{0.2}SnS₄, Cu₂Fe_{0.6}-Co_{0.4}SnS₄, Cu₂Fe_{0.4}Co_{0.6}SnS₄ Cu₂Fe_{0.2}Co_{0.8}SnS₄ and Cu₂CoSnS₄ powder samples were recorded in the frequency range 100–1800 cm⁻¹ using a micro-Raman Renishaw system 1000 equipped with a microscope Leica-DMLM. The spectra data were collected at room temperature with laser line of 633 nm and laser power of ~1 mW.

3. Results and discussion

3.1. Crystal structure

The stannite structure-type consists of a *ccp* array of sulfur atoms with metal atoms occupying one half of the tetrahedral voids. $Cu_2Fe_{0.8}Co_{0.2}SnS_4$ and $Cu_2Fe_{0.60}Co_{0.40}SnS_4$ were resolved by single-crystal X-ray diffraction. Both phases are isostructural and adopted the three-dimensional stannite-type structure. Cu-S distances ranged from 2.3232(10) to 2.307(12) Å and were close to the tetrahedral covalent radii evaluated by Pyykkö (Cu-S: 2.313 Å) [14]. These distances were also consistent with the bond lengths in phases of $Cu_2Mn_{0.4}Fe_{0.6}SnS_4$ (2.3298 Å),



Fig. 2. X-ray powder diffraction patterns of $Cu_2Fe_{1-x}Co_xSnS_4$ (x = 0.2, 0.4, 0.6 and 0.8).



Fig. 3. Final Rietveld refinement plot of Cu₂Fe_{0.6}Co_{0.4}SnS₄. Observed (open circles), calculated (line) and difference profile of X-ray diffraction are plotted.

Cu₂Mn_{0.2}Co_{0.8}SnS₄ (2.3452 Å) and Cu₂MnGe_{0.55}Sn_{0.45}S₄ (2.307–2.348 Å) [4,5,15]. The tetrahedral MS₄ (M = Fe, Co) has M–S bond distances in Cu₂Fe_{0.8}Co_{0.2}SnS₄ and Cu₂Fe_{0.60}Co_{0.40}SnS₄ of 2.329(2) and 2.327(2) Å, respectively. These distances are consistent with the bond lengths in Cu₂Mn_{0.4}Co_{0.6}SnS₄ (Mn/Co–S: 2.3302 Å) [4]. Sn–S bond distances in the tetrahedral SnS₄ are 2.414(2) and 2.415(2) Å for Cu₂Fe_{0.8}Co_{0.2}SnS₄ and Cu₂Fe_{0.60}-Co_{0.40}SnS₄, respectively. These distances are consistent with the bond lengths are consistent with the distances are consistent

The crystal structure of Cu₂Fe_{0.8}Co_{0.2}SnS₄ and Cu₂Fe_{0.60-} Co_{0.40}SnS₄ can be represented by the cation-centered tetrahedral, MS_4 (with M = Fe, Co, Cu and Sn), arranged in such a way that each sulfur atom is surrounded by four metal atoms. All polyhedra are oriented in the same direction and connected to each other at the corners, as illustrated in Fig. 1. The main features in the crystal structure of $Cu_2Fe_{0.8}Co_{0.2}SnS_4$ and $Cu_2Fe_{0.60}Co_{0.40}SnS_4$ are expected to be associated with the geometry of the MS₄ tetrahedral. The degree of distortion was evaluated using the distortion indices (DI) defined by Baur and Robinson [16,17]. The distortion can be measured by the indices of both the Edge-Length Distortion (ELD) and the tetrahedral angle variance (TAV) (see Table 3). The SnS₄ tetrahedron only shows a slight distortion (ELD <0.2%), indicating a near-ideal tetrahedra. The TAV distortion indices were <0.10%, with S-Sn-S angles ranging from 109.11(11)° to 109.59(4)°. The tetrahedral of (Fe,Co)S₄ was the most distorted polyhedral (ELD ~2% from the ideal tetrahedron).

3.2. X-ray powder diffraction, magnetic behavior and compositional characterization

The XRD patterns of the polycrystalline Cu₂Fe_{1-x}Co_xSnS₄ phases were subject to Rietveld refinement and were fully indexed in the $I\overline{4}2m$ space group (Fig. 2). Fig. 3 shows a representative refined pattern. The final structural parameters are summarized in Table 4. No secondary phases or impurity peaks were detected in XRD pattern of Cu₂Fe_{1-x}Co_xSnS₄. The volume of cell lattice increased gradually with increasing iron concentration, in line with the effective ionic radii of the tetrahedral Fe²⁺ (0.63 Å) and Co²⁺ (0.58 Å) cations reported by Shannon (for a high-spin configuration). The chemical compositions of the powder samples were determined using EDS analysis on polished surfaces of sample pellets. The backscattered image and EDS analysis (chemical maps of several areas) revealed that the samples were uniform throughout the scanned region.

Fig. 4 shows the zero-field-cooled (ZFC)/field-cooled (FC) magnetization cycle, performed under a low magnetic field (5000e) for the Cu₂Fe_{0.4}Co_{0.6}SnS₄ phase. In the magnetization cycle plot, an arrow peak can be seen, representing susceptibility at T_N~14 K (Nèel temperature). Such behavior is characteristic of antiferromagnetic interactions, in agreement with the reported results for Cu₂Mn_{0.6}Co_{0.4}SnS₄ [4]. The paramagnetic regime was analyzed well above the magnetic transition temperature and under a high applied field (10 kOe). The inset of Fig. 4 presents the inverse susceptibility, $1/\chi$, fitted by a classical Curie–Weiss relation

Table	4
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Cell parameters and Rietveld refinement data for Cu₂Fe_{1-x}Co_xSnS₄.

Phase	Cu ₂ Fe _{0.8} Co _{0.2} SnS ₄	Cu ₂ Fe _{0.6} Co _{0.4} SnS ₄	Cu ₂ Fe _{0.4} Co _{0.6} SnS ₄	Cu ₂ Fe _{0.2} Co _{0.8} SnS ₄
Space group	I42m	1 4 2m	I I 2m	I I 2m
a (Å)	5.4251(1)	5.4121(1)	5.4088(2)	5.4047(2)
c (Å)	10.8209(4)	10.8385(3)	10.8058(7)	10.7994(9)
Volume (Å ³)	318.478(5)	317.469(2)	316.125(4)	315.459(4)
R _{wp}	8.024	4.769	5.196	6.023
R _b	8.073	6.475	5.625	5.935
Rexp	2.576	2.473	2.226	2.219



Fig. 4. A representative zero field cooled/field cooled magnetization cycle at H=500 Oe of $Cu_2Fe_{0.4}Co_{0.6}SnS_4$. The insert shows the inverse susceptibility at the paramagnetic state at H=10 kOe fitted by a Curie–Weiss law.

Table 5			
Magnetic data	for C	$u_2Fe_{1-x}C$	Co _x SnS ₄ .

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Phase	μ _{theo} (μ _B) ^a	μ _{eff} (μ _B)	θ (K)	T _N (K)
Cu ₂ Fe _{0.8} Co _{0.2} SnS ₄	5.43	5.24	-85	8
Cu ₂ Fe _{0.6} Co _{0.4} SnS ₄	5.37	5.16	-158	10
Cu ₂ Fe _{0.4} Co _{0.6} SnS ₄	5.31	5.10	-185	14
Cu ₂ Fe _{0.2} Co _{0.8} SnS ₄	5.26	4.82	-143	17

^a $\mu_{theo} = \sqrt{4S(S+1) + L(L+1)}$

 $\chi = C/(T-\Theta)$, in the range of 150 K < T < 300 K, from which the effective moment μ_{eff} and the Curie–Weiss temperature Θ were obtained (see Table 5). The observed effective moments were close



3.3. Raman scattering analysis

From a vibrational point of view, the representation of the optical phonon modes found in the stannite-type crystal structure ($I\overline{4}2m$ space group) can be written as $\Gamma = 2A_1 \oplus A_2 \oplus 2B_1 \oplus 4B_2 \oplus 6E$ [18,19]. Of these modes, A_1 is the principal, having the two strongest lines in the Raman spectrum in accordance with that observed in chalcopyrite, which is closely related to CFTS and CCTS [20]. B_2 and E modes are also active in IR and show LO-TO splitting due to their polar character. The unique mode that is not active in Raman is A_2 . The vibrations of the A_1 mode can be viewed as a "breathing" mode of SnS₄ and MS₄ (M = Fe²⁺ y Co²⁺) tetrahedra. This vibrational mode can be understood as the expansion or contraction of the M–S bonds, simultaneously triggered by sulfur atoms placed at the vertices of the tetrahedra.

Fig. 5 shows fitting of the Raman spectrum with Lorentzian curves for Cu₂Fe_{1-x}Co_xSnS₄ solid solutions between 200 and 400 cm⁻¹. This is the region where main changes in the spectrum take place. The Raman spectrum of CFTS (Cu₂FeSnS₄ end-member) shows two peaks at 319 and 287 cm⁻¹, which can be assigned to the A_1 vibration mode as an analogy to stannite, aside from a weak contribution at 351 cm⁻¹assigned to the B_2 mode. The frequency of these peaks is also consistent with the main Raman peaks reported in CFTS [18,19,21]. The Raman spectrum of CCTS is characterized by two main peaks that also can be assigned to the A_1 vibration mode but are displaced to higher energies at 326 and 289 cm⁻¹, together with three additional contributions at 268, 348 and 368 cm⁻¹. The peaks at 268 cm⁻¹. All peaks are consistent with the peaks reported in CCTS [4,22,23].

The Raman spectra of $Cu_2Fe_{1-x}Co_xSnS_4$ (x = 0.2, 0.4, 0.6 and 0.8)



Fig. 5. Raman spectrum of Cu₂Fe_{1-x}Co_xSnS₄with the different contributions as deduced from the fitting of the different peaks with lorentzian curves (green lines).

Table 6

Frequency and proposed mode assignment of Raman peaks from solid solutions $Cu_2Fe_{1-x}Co_xSnS_4$ compared with experimental data reported.

x values					Symmetry	References	
1.0	0.8	0.6	0.4	0.2	0.0		
268	255	262	262	264	_	B ₂	[18,19]
289	281	287	287	285	287	A_1	[18-22]
_	_	_	_	308	_	B_2	[18,19,23]
326	324	321	320	320	319	A_1	[18-23]
-	-	332	332	-	-	B_1	[23]
348	346	_	_	345	_	Ε	[18]
_	_	356	351	360	351	B_2	[18,19,23]
368	_	_	370	_	-	B_2	[22]

solid solutions show that there is a variation in the frequency of the main A_1 vibration mode at ~320 cm⁻¹, together with a decrease in the intensity of the secondary mode at ~285 cm⁻¹. This decrease is proportional to the chemical iron content. Fitting all spectra gives evidence of weak additional contributions. Table 6 summarizes the frequency, FWHM and vibrational modes proposed for experimental peaks from the data reported in the literature for stannite. The broadening of the main peaks found in Cu₂Fe_{1-x}Co_xSnS₄ (x = 0.2, 0.4, 0.6 and 0.8) solid solutions is attributed to disorder effects due to chemical substitutions in M crystallographic positions.

Fig. 6 shows a plot of the frequency and FWHM versus *x* values of the main A_1 vibration mode in Cu₂Fe_{1-*x*}Co_{*x*}SnS₄. As shown, the peak position has inflections at x = 0.6 with two linear correlations. The second line has a major pendent which can be attributed to a high cobalt chemical content (x > 0.6). Importantly, all of the



Fig. 6. Frequency and FWHM of the main A_1 peak of the Raman spectra of $Cu_2Fe_{1-x}Co_xSnS_4$.

4. Conclusions

In this paper, we presented the effect of the partial substitution of Fe with Co in Cu₂Fe_{1-x}Co_xSnS₄ phases. Cu₂Fe_{0.8}Co_{0.2}SnS₄ and Cu₂Fe_{0.60}Co_{0.40}SnS₄ crystallize in the tetragonal stannite-type structure. This structure can be represented by cation-centered tetrahedra of MS₄ (with M = Fe, Co, Cu and Sn), where all polyhedra are oriented in the same direction and are connected at the corners. The (Fe,Co)S₄ tetrahedron presented the highest distortion in agreement with the disorder in the occupation of Fe²⁺ and Co²⁺ cations (at the same crystallographic site 2a). The oxidation states of the metals were confirmed by temperature-dependent magnetization measurements. The XRD patterns were fully indexed in the $I\overline{4}2m$ space group. The Raman spectra were dominated by two peaks that appear in the 280–340 cm⁻¹ spectral region, and the broadening of this peak can be attributed to the disorder effects related to (Fe,Co)S₄ tetrahedra.

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