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Cu₂ZnSnSe₄ formation and reaction enthalpies in molten NaI starting from binary chalcogenides

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Abstract The present study deals with chemical reactions and enthalpies during the synthesis of Cu₂ZnSnSe₄ (CZTSe) from CuSe, SnSe, and ZnSe in molten NaI as flux material in closed degassed ampoules. Differential thermal analysis (DTA) at heating rates 5 °C min⁻¹ and cooling rates 10 °C min⁻¹ were used for the determination of temperatures of phase transitions and/or chemical reactions. XRD and Raman analyses confirmed that the formation of CZTSe starts already at 380 °C after the melting of Se that deliberates from the transformation of CuSe to Cu_{1.8}Se, and the CZTSe formation process impedes to a great extent due to the presence of solid NaI. After the melting of NaI, the formation of CZTSe is completed. For the determination of enthalpy values, the calibration with pure NaI was performed. The thermal effects and enthalpies were compared with the available known thermodynamical values. The specific enthalpy of exothermic Cu₂ZnSnSe₄ formation at 661 °C in NaI -36 ± 3 kJ mol⁻¹ was determined experimentally for the first time. Ternary compound Na₂SnSe₃ was formed during the synthesis process. NaI·2H₂O, if present in NaI, was found to be a critical issue in the synthesis process of CZTSe monograin powders in molten NaI—it gave rise to the formation of oxygen-containing by-

products Na₂SeO₄ and Na₂Cu(OH)₄. The complete dehydration of NaI·2H₂O at $T \leq 70$ °C in vacuum is necessary to avoid the formation of oxygen-containing compounds.

Keywords Cu₂ZnSnSe₄ · Monograin material · Formation enthalpy · NaI

Introduction

The latest achieved efficiency with hydrazine slurry approach for Cu₂ZnSn(Se, S)₄ solar cells of 12.6 % belongs to scientific group as reported in [1], working for IBM company. However, only our group works mostly with syntheses of CZTSe, CZTS, or CZTSSe, based on flux materials. This method is preferable due to its easy preparation and up-scaling requirements. It is known that the use of suitable flux material in sufficient amounts leads to single-crystalline Cu₂ZnSnSe₄ powder growth. During the synthesis process, the liquid phase acts as a particle-repelling agent for precursors, preventing the sintering. The driving force in the monograin powder growth is the difference in surface energies of crystals of different sizes. Our previous reports have shown that the growth of single-crystalline powder grains takes place at temperatures above the melting point of the used flux material [2]. The liquid phase of a flux is also advantageous for the synthesis of multi-component compounds, allowing fast diffusion of constituent elements through liquid phase and providing therefore uniform composition of absorber materials for solar cells [3]. The requirement of the process is that the synthesis of Cu₂ZnSnSe₄ (CZTSe) monograin materials must result in the homogeneous single-phase material [4]. The flux material should have low melting temperature and high solubility in water, allowing an easy separation of the

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powder particles from the flux. There are several suitable flux salts such as KI, NaI, and CdI_2 available for the synthesis, monograin growth, or re-crystallization of the absorber materials. In the previous papers [5, 6], we presented the results of studies of $\text{Cu}_2\text{ZnSnSe}_4$ formation in molten CdI_2 and KI. NaI is a compound with about 30° lower melting temperature than KI, allowing to reduce the synthesis temperature. Its chemical properties are close to KI and the non-toxicity of it is an advantage if compared with CdI_2 . The present study deals with the possible chemical reactions between the binary precursor compounds-CuSe, SnSe, and ZnSe-in molten NaI and the chemical interactions of them with NaI, in order to find the critical issues and solutions for $\text{Cu}_2\text{ZnSnSe}_4$ synthesis. The aim of this study is to find suitable preparation conditions for the synthesis of $\text{Cu}_2\text{ZnSnSe}_4$, starting from binary chalcogenide compounds. The evaluation of enthalpies of syntheses allows to understand more clearly the syntheses process and chemical pathway. However, similar results of DTA curves from via syntheses of CZTSe material in literature are not available.

Experimental

The quaternary $\text{Cu}_2\text{ZnSnSe}_4$ powder materials were synthesized from binary CuSe, ZnSe, and SnSe precursor powders in molten NaI in sealed quartz vacuum ampoules. Before starting the syntheses, it is very important to have dehydrated NaI, due to its trend to form $\text{NaI} \cdot 2\text{H}_2\text{O}$. After heating under continuous vacuum pumping for 4 h up to 370°C there was no water emission detected by mass spectrometry (MS). For the enthalpy calculations, the DTA calibration was performed. The melting and solidification effects of pure NaI (with the molar enthalpy of fusion $23.679 \text{ kJ mol}^{-1}$ at its melting point) were selected as standard. NaI is the preferable substance for DTA calibration, because all the studied samples consist mostly of the flux material (NaI). The melting point of NaI is at the same temperature region where the most of the thermal effects in investigated samples were detected. The maximal deviations in calibration experiments were considered as 8 % and were used for the evaluation of enthalpy deviations. The experiments and calibration were done in evacuated quartz ampoules with the aim to get a transformation constant to be able to transform the data for the open system and compare the gained results with those given in literature. The quartz ampoules were designed with cylindrical base and fitted to cylindrical thermocouple to enlarge the contact with thermocouple and be able to have precise measurements for enthalpy evaluation. Fine grinding in a mortar mixed the precursors in compliance with the stoichiometry of CZTSe. The amounts of

compounds used for the mixtures were 0.00037645 mol CuSe, 0.00020637 mol ZnSe, 0.00020638 mol SnSe, and 0.00083389 mol NaI. In the mixtures, it resulted in following molar ratios: CuSe + NaI (1.85:4), ZnSe + NaI (1:4), SnSe + NaI (1:4), CuSe + SnSe + NaI (1.85:1:4), and CuSe + ZnSe + SnSe + NaI (1.85:1:1:4). DTA setups (Thermogravimetric Analyzer Labsys 1600, Setaram Instrumentation, Caluire, France) were used for the detection of the phase changes and the interactions between the initial binaries and the flux material. As a reference for the DTA, empty quartz ampoule was used. The applied heating rates were 5°C min^{-1} and cooling rates $10^\circ\text{C min}^{-1}$. According to the thermal effects found in DTA curves, identical larger samples (1 g) of the mixtures were prepared for Raman and XRD analyses. The samples were heated for 4 h at temperatures few degrees higher than the observed thermal changes in the DTA curves, and then quenched in water.

Room temperature Raman spectra were recorded using a Horiba's LabRam HR800 high-resolution spectrometer (France) equipped with a multichannel CCD detection system in backscattering configuration. Micro Raman measurements were performed using incident laser light of 532 nm focused on a $1\text{-}\mu\text{m}$ spot of the studied sample. In order to get true results, at least 5 Raman spectra were taken from different spots for every sample. XRD measurements were performed using a Bruker D5005 diffractometer, (Karlsruhe, Germany). For analysis of the XRD patterns, the ICDD PDF-4 + 2009 database was used.

After Raman and XRD analyses of non-washed samples, the formed solid phases in the samples were separated from the soluble part of flux material by washing with distilled water several times (7–10) using ultrasonic bath for agitation until washing water became transparent. The separation of flux material (NaI) and other soluble phases after syntheses from samples quenched at different temperatures of mixture CuSe + ZnSe + SnSe + NaI gave the possibility to record more clear spectra of Raman and XRD pattern of insoluble phases in water, by-products, and CZTSe formation.

Results and discussion

Dehydration of NaI

DTA heating/cooling curves of pure NaI are shown in Fig. 1. Only an endothermic peak at 660°C (melting) in the heating curve and an exothermic peak at 639°C (solidification) in the cooling curve of average signal $7,996 \mu\text{Vs}$ are seen. Besides cubic NaI (Fm-3 m (225) $a = 6.47 \text{ \AA}$), triclinic $\text{NaI} \cdot 2\text{H}_2\text{O}$ (P-1(2) $a = 7.146$ and $b = 7.169$, $c = 6.029 \text{ \AA}$) was detected in all samples by

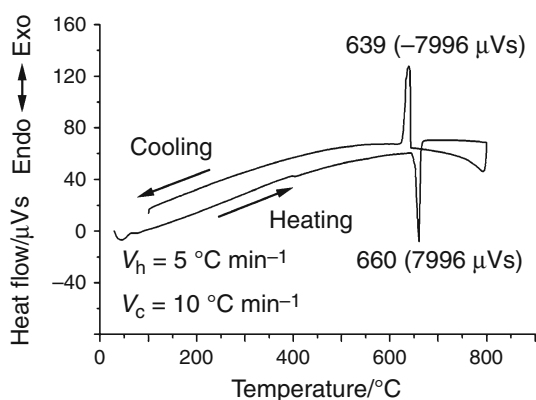
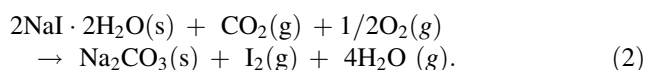
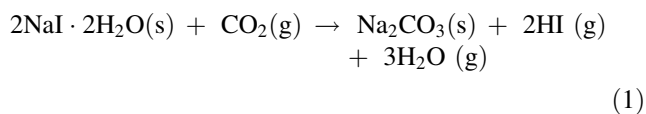


Fig. 1 DTA curves of NaI

XRD. Corresponding Raman peaks of NaI·2H₂O were found experimentally at 82, 90, 95, 99, 107, 115, 122, 135, 138, 150, 187, 194, 222, 230, 244, 323, 353, and 419 cm⁻¹. It is known that NaI is very hygroscopic, and NaI·2H₂O can be easily formed when handling NaI in air. We performed thermo-gravimetric (TG) study of NaI dehydration using mass spectrometry (MS) for the gas-phase analysis. In the TG curve of NaI (see Fig. 2) before dehydration, there is seen a mass loss starting at onset point of 35 °C with peak maximum at 51 °C and the offset point at 69 °C. MS analysis confirmed that this mass loss is caused by H₂O emission. On the basis of the paper [7], where it is reported that in the NaI-H₂O system NaI·2H₂O exists in the temperature region of -13.5 °C to 68 °C (or 68.2 and $P_{\text{H}_2\text{O}} = 6.32$ kPa [8]), this peak of mass loss is attributable to the NaI·2H₂O decomposition. The authors, as described in the article [7], studied extra pure grade NaI and the crystalline hydrate of (NaI·2H₂O) by differential barothermal analysis method using mass spectrometry to determine the composition of the gas phase and the partial pressures of gas-phase components. They found that the crystal hydrate NaI·2H₂O can be successfully dehydrated already at room temperature in vacuum. The vapor pressure above dehydrated NaI was low and nearly constant during heating up to 600 °C. By their study, NaI·2H₂O reacted with carbon dioxide and not with oxygen only in the gas phase during heating. They proposed that heating of NaI·2H₂O in the mixture of carbon dioxide and oxygen should lead to the formation of sodium carbonate by the reactions (1) and/or (2) [7]:



The reaction (2) shows the way how iodine can be released from NaI·2H₂O. Sodium carbonate, in turn, can

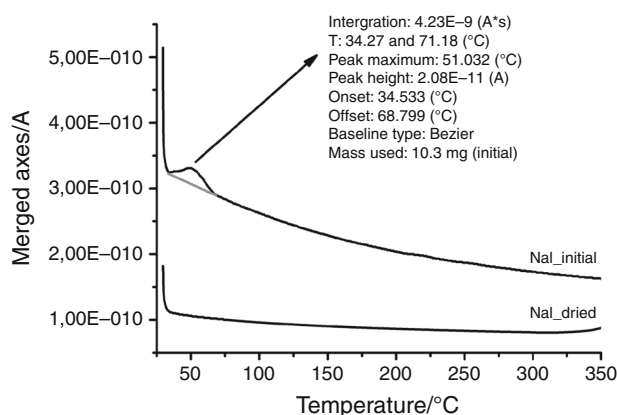
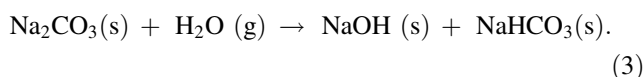


Fig. 2 TG curves of initial and dehydrated NaI

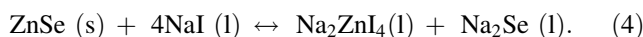
react with water vapor according to the well known scheme [7]:



The reaction (3) is more likely at higher temperatures, up to sodium carbonate decomposition ($T > 600$ °C). In the opinion of the authors [8], this reaction is responsible for the contamination of NaI with OH⁻ groups. During rehydration of NaI, the hydroxyl groups are captured by water molecules to give stable aqua complexes, which decompose only above 180 °C.

Quasi-binary systems

DTA heating/cooling curves of the mixtures CuSe + NaI (black), ZnSe + NaI (gray), and SnSe + NaI (gray) are presented in Fig. 3, and the phases found by XRD and Raman analyses are summarized in Table 1. In the heating curves of quasi-binary systems ZnSe + NaI and SnSe + NaI (Fig. 3 a gray lines), endothermic peaks of melting at 659 °C (with signals 727 μVs for ZnSe + NaI and 633 μVs for SnSe + NaI) are partly covered by some exothermic processes occurring during the melting of the mixtures since the melting of pure NaI of the equal amount gave a signal of 7,996 μVs. This exothermic effect can be calculated as 7,269 μVs (727–7,996 = -7,269 μVs) for the mixture of ZnSe + NaI. This value corresponds to the difference of solvation energy to break the bonds and to form new bonds in liquid phase. Since the solubility of ZnSe in NaI is not determined, the value of heat effect cannot be expressed in kJ mol⁻¹. The formation of a complex between liquid NaI and ZnSe (4) can be proposed similarly [9] as follows:



The similar value of exothermic effect for the complex formation in the SnSe + NaI mixture by DTA heating curve can be calculated as 633–7,996 = -7,363 μVs.

Fig. 3 DTA curves of the: **a** ZnSe + NaI, SnSe + NaI (gray lines), CuSe + NaI black line, and a part of phase diagram of Cu-Se system on the right side of (a), CuSe + SnSe + NaI (b) and the mixture for synthesis of quaternary CZTSe (c)

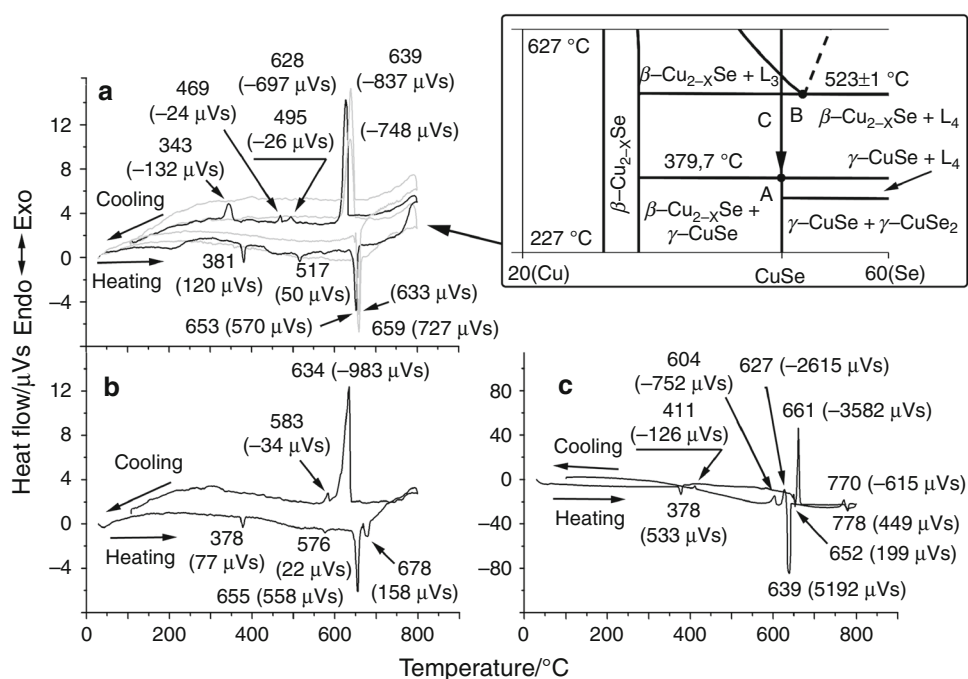


Table 1 Phases found by XRD (symmetry, space group, lattice parameters (Å)) and by Raman (Raman shift (cm⁻¹)) in the studied samples, according to the detected effects in DTA curves

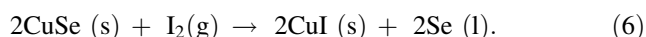
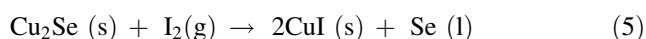
Phase	Raman shift/cm ⁻¹ and ref.	NaI + CuSe	NaI + CuSe + SnSe	NaI + CuSe + SnSe + ZnSe
CuSe, Hexagonal P63/mmc (194), $a = 3.94600$, $c = 17.17800$	—	Heating (380–660 °C)	Heating (380–680 °C)	Heating (380–790 °C)
Cu _{1.82} Se (Berezianite), Cubic F-43 m (216), $a = 5.72200$	263 [12]	Cooling (515–495 °C)	Cooling (635–550 °C)	
CuI (Marshallite), Cubic F-43 m (216), $a = 6.08474$	122, 139 [exp.]			
ZnSe (Stilleite), F-43 m (216) $a = 5.66800$	204 251 [22]	—	—	
CZTSe, tetragonal I-42 m (121) $a = b = 5.73323$, $c = 11.41811$	81, 171, 191*, 194*, 196, 231 [5]			
Na ₂ Cu(OH) ₄ , Orthorhombic, Pna21 (33) $a = 6.7500$, $b = 6.72600$, $c = 8.99300$	—			
Na ₂ SeO ₄ , Orthorhombic, Fddd (70) $a = 10.17100$, $b = 12.58700$, $c = 6.10380$	—			
SnSe, orthorhombic, $a = 11.50700$, $b = 4.15000$, $c = 4.48000$	130, 150 [23]	—	Only by heating at 580 °C	
SnSe ₂ , hexagonal, primitive P-3m1 (164), $a = b = 3.80400$, $c = 6.15100$	186 [15]	—	Only by heating at 380 °C	
Cu ₂ SnSe ₃	178, [20] 180 236 [5]	—	Heating (380–680 °C) Cooling (635–550 °C)	Only by heating at 380 and at 790 °C
Se	240 [exp.]	—	—	
Na ₂ SnSe ₃ , Monoclinic, P21/c (14) $a = 7.24400$, $b = 16.21800$, $c = 6.17400$	—	—	—	Only by heating at 790 °C

* Shift to the lower peak values is similar to the solid solutions [27]

The exothermic peaks in the cooling curves of ZnSe + NaI and SnSe + NaI in the vicinity of the melting and solidification point of pure NaI at 639 °C are recorded as 748 and 837 μ Vs, respectively. The thermal effects of reversible to those processes described above can be calculated as 7,248 μ Vs for ZnSe + NaI mixture and 7,159 μ Vs for SnSe + NaI mixture. The enthalpy values of forward and reversible processes are rather close ($-7,269/7,248$ μ Vs for ZnSe + NaI and $-7,363/7,159$ μ Vs for SnSe + NaI). The samples of those mixtures investigated after annealing at 660 °C do not show any new formed phases. From this phenomenon, it can be derived that the complex formation takes place only in the liquid phase and it is a reversible process.

The detected peak positions of thermal effects in CuSe + NaI mixture are marked in Cu-Se phase diagram from the Ref. [10] (see insert in Fig. 3 a right side). The DTA peaks and enthalpies in the CuSe + NaI system can be attributed to the phase changes and reactions as follows:

The thermal effect at 381 °C in the heating curve (Fig. 3 a right side point A (379.7 °C), with detected endothermic signal of 120 μ Vs, corresponds to the formation of Cu_{2-x}Se due to the peritectic decomposition of CuSe [10]. The formation of Cu_{2-x}Se phase was confirmed by Raman peak at 263 cm⁻¹ [11]. XRD pattern of the sample quenched at 380 °C confirmed also the transformation of CuSe to Cu_{1.8}Se (berzelianite). At the same time, the formation of CuI was found by XRD analysis and Raman spectra with peaks at 122, and 139 cm⁻¹. The reference Raman spectra of α , β , and γ modifications of CuI with Raman shifts at 93, 122, and 139 cm⁻¹ were experimentally measured by us and found to be identical with each other. The formation of CuI can be thermodynamically possible if iodine, released from NaI, see reaction (2), takes part in the formation of CuI described by the following reactions (5, 6). The thermodynamic calculations were made on the bases of data from [12–14]. The value of Gibbs energy change ΔG is negative ($\Delta G < 0$); for the reaction (5) in the region of temperatures 0–774 °C, the ΔG is -95 kJ mol⁻¹ at 0 °C; -38 kJ mol⁻¹ at 380 °C (the quenching temperature of the sample); and almost 0 kJ mol⁻¹ at 774 °C; for the reaction (6), the ΔG is -81 kJ mol⁻¹ at 0 °C; -37 kJ mol⁻¹ at 380 °C; and -17 kJ mol⁻¹ at 800 °C:



The thermal effect at 517 °C in the heating curve with detected signal of 50 μ Vs can be attributed to the formation of a liquid phase similar to the L₃ [12] (see insert in Fig. 3, right side, point B). The temperature of the liquid phase L₃ formation (517 °C) is lower than the temperature of monotectic point in Cu-Se phase diagram (523 °C) probably due to sodium and copper iodide impurities.

653 °C corresponds to the melting of NaI + CuSe mixture. The melting temperature of a substance can be reduced due to the added impurities. CuSe in NaI increases the entropy, and the melting of the mixture takes place at a much lower temperature than pure NaI. The accompanied endothermic melting signal of 570 μ Vs is covered by the thermal effect of another exothermic process with signal value of $-7,426$ μ Vs. It could be some complex formation in the formed liquid phase due to the solvation of CuSe in NaI. The thermal effect at 628 °C in the cooling curve with signal of -697 μ Vs can be attributed to the solidification of NaI + CuSe. This signal is covered by another signal of 7,299 μ Vs that could be accompanied by the reversible endothermic precipitation of CuSe from NaI.

The thermal effects at 495 °C (-26 μ Vs) and 469 °C (-24 μ Vs) (in sum of $24 + 26 = 50$ μ Vs) in the cooling curve (see insert in Fig. 3, right side, where arrow C is crossing the liquidus line (precipitation of Cu_{2-x}Se) and temperature of monotectic point (formation of liquid L₄) and moving to point A) correspond to the reversible process detected in the heating curve at 517 °C (50 μ Vs).

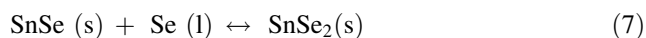
The thermal effect at 343 °C (-132 μ Vs) in cooling curve corresponds to the peritectic process detected in the heating curve at 381 °C (see text above) [12]. The temperatures are shifted to lower side probably due to impurities.

Ternary and quaternary systems

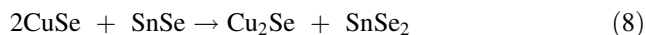
The DTA heating/cooling curves of the CuSe + SnSe + NaI and CuSe + ZnSe + SnSe + NaI mixtures are presented in Fig. 3 b, c, respectively. The found phases in the heated samples of the non-washed mixtures are given in Table 1.

The endothermic peak around 378 °C occurring in heating curves of the both mixtures (with thermal effects of 77 and 533 μ Vs correspondingly) is seen also in the DTA heating curve of the quasi-binary system CuSe + NaI (381 °C) presented in Fig. 3 a. Therefore, we attribute this peak to the peritectic process at temperature of 379.7 °C in CuSe binary system, the CuSe phase transformation, and decomposition to Cu_{2-x}Se + Se as shown in the phase diagram of CuSe in [12]. Cu_{1.8}Se (berzelianite) is confirmed by XRD analysis, and Cu_{2-x}Se phase was detected by Raman peak at 263 cm⁻¹ [13]. At this temperature, CuI forms in both systems as described above (see reactions 5–6), and it is confirmed by XRD data and Raman shifts at 122 and 139 cm⁻¹ (see Table 1). We determined also experimentally Raman shifts of elemental Se for reference. They were found at 138, 233, and 238 cm⁻¹. The presence of SnSe₂ in the XRD pattern and in Raman spectra at 186 cm⁻¹ [15] can be expected from reaction (7) between

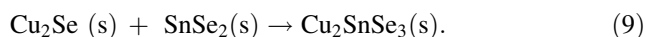
SnSe and Se, released from CuSe (detected by Raman peak of elemental Se at 240 cm^{-1}), as follows:



$\Delta G < 0$; at $0\text{ }^\circ\text{C}$ it is -25 kJ mol^{-1} , at $380\text{ }^\circ\text{C}$ (the quenching temperature of the sample) $\Delta G = -13\text{ kJ mol}^{-1}$ and it is almost 0 kJ mol^{-1} at $719\text{ }^\circ\text{C}$ [16–18]. Also for the direct reaction:



$\Delta G < 0$; at $0\text{ }^\circ\text{C}$ it is -10 kJ mol^{-1} , at $380\text{ }^\circ\text{C}$ -12 and -16 kJ mol^{-1} at $800\text{ }^\circ\text{C}$ [16–18]. Then Cu_2Se and SnSe_2 react with each other forming Cu_2SnSe_3 :



Cu_2SnSe_3 formation in the sample quenched at $380\text{ }^\circ\text{C}$ was confirmed by XRD and Raman measurements (Raman peaks at 178 [19], 180 , and 236 cm^{-1} [3]).

In the mixture of $\text{CuSe} + \text{ZnSe} + \text{SnSe} + \text{NaI}$, the XRD analysis does not confirm the formation of CZTSe at $380\text{ }^\circ\text{C}$; however, it was detected by Raman spectroscopy at 173 , 196 , and 236 cm^{-1} [4]. As the main CZTSe formation process occurs with melting of NaI and only a small amount of it forms at $380\text{ }^\circ\text{C}$ (even not seen in the XRD pattern), then we believe that the formation of CZTSe at $380\text{ }^\circ\text{C}$ is probably initiated by the release and melting of Se. Formed liquid phase between solid particles allows fast diffusion of reaction components, like in ceramics, where molten salts have been used as additives to enhance the rates of solid state reactions, due to much higher diffusion rates between reaction components in the molten media [20]. Otherwise, in the presence of a big amount of solid NaI, only the solid-state reactions could be expected at this temperature. Up to the melting of NaI (peak at $661\text{ }^\circ\text{C}$ in the DTA curve) unreacted Cu_{2-x}Se , ZnSe , SnSe , and SnSe_2 are detected in Raman spectra by their characteristic peaks at 263 , 254 cm^{-1} [11, 21] and 129 , 150 cm^{-1} [22], and their reflections are present in the XRD pattern. Also, Na containing by-products $\text{Na}_2[\text{Cu}(\text{OH})_4]$ and Na_2SeO_4 were detected in the sample quenched at $380\text{ }^\circ\text{C}$. The formation of these compounds could be a sign of the presence of $\text{NaI} \cdot 2\text{H}_2\text{O}$ in NaI. $\text{Na}_2[\text{Cu}(\text{OH})_4]$ and Na_2SeO_4 phases were found by XRD, and as we could not find the Raman data of these compounds in literature, we synthesized these compounds for reference. The $\text{Na}_2[\text{Cu}(\text{OH})_4]$ compound was synthesized as described in [23], and Na_2SeO_4 by stoichiometric oxidation of SeO_2 with H_2O_2 and mixing with NaOH in a glove box under nitrogen atmosphere. The synthesized crystals were confirmed by XRD. The experimentally recorded Raman peaks of $\text{Na}_2[\text{Cu}(\text{OH})_4]$ were at 219 , 311 , 438 , and 443 cm^{-1} and at 120 , 338 , 362 , 424 , 454 , and 477 cm^{-1} for Na_2SeO_4 ; however, in the Raman spectra of the studied mixtures, these compounds were not

found by their characteristic Raman peaks. According to Table 1, the thermal effects can be described as follows:

- The endothermic peak at $576\text{ }^\circ\text{C}$ ($22\text{ }\mu\text{Vs}$) in the heating curve of the mixture $\text{CuSe} + \text{SnSe} + \text{NaI}$ (see Fig. 3 b) and at $583\text{ }^\circ\text{C}$ ($-34\text{ }\mu\text{Vs}$) in the cooling curve can be attributed to the eutectic point of Cu_2SnSe_3 - SnSe_2 [24].
- Endothermic melting of NaI ($7,996\text{ }\mu\text{Vs}$, see Fig. 1) is seen at $655\text{ }^\circ\text{C}$ as a summary thermal effect with value of $558\text{ }\mu\text{Vs}$ due to its coverage by an exothermic effect of value $-7,438\text{ }\mu\text{Vs}$ ($-7,996 + 558 = -7,438$). The process can be attributed to the Cu_2SnSe_3 formation as reaction (9) with enthalpy of $-32 \pm 3\text{ kJ mol}^{-1}$ at this temperature. Since the enthalpy value is not large, it is more believable that the formation of ternary compound from Cu_2Se and SnSe_2 occurs in the liquid phase. Reversible process ($30 \pm 2\text{ kJ mol}^{-1}$) can be calculated from the NaI solidification effect of $983\text{ }\mu\text{Vs}$ at $634\text{ }^\circ\text{C}$, where it is covered by an endothermic process of $7,013\text{ }\mu\text{Vs}$.
- The melting enthalpy of Cu_2SnSe_3 1 kJ mol^{-1} was determined only in the first heating curve at $678\text{ }^\circ\text{C}$ ($158\text{ }\mu\text{Vs}$). The experimental heat of fusion of Cu_2SnSe_3 has not been reported before. However, it is not detected in the cooling cycle, the reason could be the overlapping of multiple thermal effects.
- The peaks in the cooling curve of $\text{NaI} + \text{ZnSe} + \text{CuSe} + \text{SnSe}$ at $604\text{ }^\circ\text{C}$ ($-752\text{ }\mu\text{Vs}$) should belong to the melting point of CuI ($T_m = 606\text{ }^\circ\text{C}$ [12, 13]) found in XRD studies (Table 1), and the exothermic peak at $411\text{ }^\circ\text{C}$ ($-126\text{ }\mu\text{Vs}$) can be attributed to the phase change of $\alpha\text{-CuI}$ to $\beta\text{-CuI}$ as reported by Rapaport and Pistorius at $408.5 \pm 1.5\text{ }^\circ\text{C}$ [25].

In the vicinity of the melting temperature of pure NaI ($660\text{ }^\circ\text{C}$) a summary endothermic effect (melting process of $199\text{ }\mu\text{Vs}$) can be seen in the heating curve of the mixture $\text{CuSe} + \text{ZnSe} + \text{SnSe} + \text{NaI}$ at $652\text{ }^\circ\text{C}$. It means that the thermal effect of NaI melting ($7,996\text{ }\mu\text{Vs}$) is covered by an exothermic effect of $7,797\text{ }\mu\text{Vs}$. The following intense exothermic interaction between compounds at $661\text{ }^\circ\text{C}$ ($-3,582\text{ }\mu\text{Vs}$) ends with the CZTSe formation. The total value of the exothermic effect for the CZTSe formation (from ternary compound and ZnSe by reaction (10)) can be calculated then as $-11,379\text{ }\mu\text{Vs}$:



From these considerations the specific enthalpy of CZTSe formation (at $661\text{ }^\circ\text{C}$) is $-36 \pm 3\text{ kJ mol}^{-1}$. This value is experimentally determined for the first time. Reversible process in cooling cycle at $639\text{ }^\circ\text{C}$ ($5,192\text{ }\mu\text{Vs}$), where the thermal effect of NaI solidification (seen at $627\text{ }^\circ\text{C}$ ($2,615\text{ }\mu\text{Vs}$)) is covered by $5,381\text{ }\mu\text{Vs}$. The total

reversible process of 10,573 μVs results in enthalpy value of $33 \pm 3 \text{ kJ mol}^{-1}$. The value differs in few kJ mol^{-1} due to the fact that the formation enthalpy depends on temperature, and by cooling, the detected effect is shifted from 661 to 639 $^{\circ}\text{C}$. Theoretically calculated formation enthalpy of CZTSe from binary precursors Cu₂Se, SnSe₂, and ZnSe is $-84.1 \text{ kJ mol}^{-1}$ [26]. If to consider that for the reaction (8) $\Delta H = -7.2 \text{ kJ mol}^{-1}$ at 661 $^{\circ}\text{C}$ [16–18] and the determined value for the reaction (9) in the mixture CuSe + SnSe + NaI (see in Fig. 3 b at 655 $^{\circ}\text{C}$) is $-32 \pm 3 \text{ kJ mol}^{-1}$, then the total experimental value of CZTSe formation starting from CuSe, SnSe, and ZnSe is $-7 + (-32) + (-36) = -75 \pm 6 \text{ kJ mol}^{-1}$ at 662 $^{\circ}\text{C}$. This means that the determined experimental value is in good agreement with the theoretically calculated. Also, it should be taken into account that CuSe, SnSe, and ZnSe were found as unreacted in the studied samples up to high temperatures (CuSe decomposition is limited due to the forming overpressure of Se in the closed ampoule, that suppresses the decomposition of CuSe). In addition, the authors want to underline, that it is complicated to predict the influence of CZTSe formation pathway starting from ternary compound Na₂ZnSnSe₃, which was also found by XRD in low concentrations at 790 $^{\circ}\text{C}$.

It was established in [24] that Cu₂ZnSnSe₄ melts incongruently at 788 $^{\circ}\text{C}$ leaving ZnSe:Cu:Sn in the solid phase. Therefore, the peaks of 449 μVs (1 kJ mol^{-1}) at 778 $^{\circ}\text{C}$ in the heating curve and of 615 μVs (2 kJ mol^{-1}) at 770 $^{\circ}\text{C}$ in the cooling curve of CuSe + ZnSe + SnSe + NaI can be attributed to the melting/solidification of CZTSe. The shift of these peaks from 788 $^{\circ}\text{C}$ to lower temperatures can be attributed to the formation of sodium-containing quaternary compound similar to CZTSe. In the Raman spectrum of the sample quenched at 790 $^{\circ}\text{C}$, the main Raman peaks of CZTSe are shifted from 196 to 194, 191 and from 173 to 171 cm^{-1} . Such shift to the lower peak values is similar to the solid solutions Cu₂ZnSn(S_{1-x}Se_x)₄ with small amounts of Cu₂ZnSnSe₄ [27] and also in our solid solutions of CZTS with Cu₂CdSnS₂ [to be published elsewhere]. The samples quenched at 790 $^{\circ}\text{C}$ show again ternary compound Cu₂SnSe₃ or Na₂SnSe₃ (178 cm^{-1}) in Raman spectra, while Na₂SnSe₃ as a possible precursor for the sodium-containing quaternary compound was found in the XRD pattern (Table 1). Besides the ternary and quaternary compounds in XRD pattern and Raman spectra with intensive peaks at 139, 150, 186, 240, 251, and 263 cm^{-1} belong to CuI, Se, SnSe, SnSe₂, ZnSe, and Cu_{2-x}Se were found. Due to the fast cooling, the re-formation of CZTSe from the melt should be incomplete in the cooling process. Overpressure of Se in the ampoule obviously avoids the complete decomposition of CuSe.

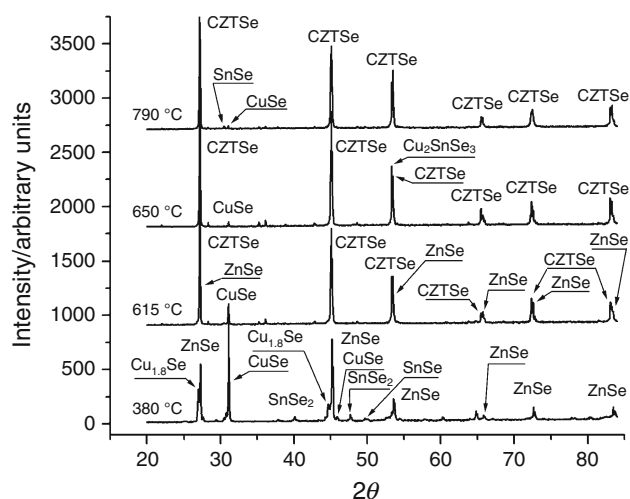


Fig. 4 XRD patterns of CuSe + ZnSe + SnSe + NaI mixtures quenched at different annealing temperatures (after washing out NaI and soluble phases with water)

All sodium-containing compounds are well soluble in water and can be removed by washing. Only CuI is poorly soluble in water (0.00042 g L^{-1} at 25 $^{\circ}\text{C}$), but it dissolves in the presence of NaI or KI by forming the linear anion $[\text{CuI}_2]^-$. Dilution of such solutions with water leads to the re-precipitation of CuI [28].

The XRD patterns and Raman spectra of the sample mixtures of CuSe + ZnSe + SnSe + NaI quenched from different annealing temperatures and washed for separation of NaI are presented in Figs. 4 and 5. As it can be seen from the experimental data, the main CZTSe formation process occurs with melting of NaI and only a small amount of it forms at 380 $^{\circ}\text{C}$ (even not seen in the XRD pattern). We believe that the formation of CZTSe at 380 $^{\circ}\text{C}$ is initiated by the release and melting of Se due to the decomposition of CuSe. Formed liquid phase between solid particles allows fast diffusion of reaction components, like in ceramics, where molten salts have been used as additives to enhance the rates of solid state reactions, due to much higher diffusion rates between reaction components in the molten media [19]. The reactions of CZTSe and Cu₂SnSe₃ formation starting after the deliberation of Se from CuSe consume the available Se, and then the reactions are inhibited after the formation of Se overpressure in the closed ampoules. Overpressure of Se suppresses the further decomposition of CuSe, and the resultant amounts of formed CZTSe and Cu₂SnSe₃ are lower than the sensitivity of XRD, even in washed samples. Also, the big amount of solid NaI between solid precursor particles inhibits the rate of CZTSe formation reaction. Therefore, the characteristic Raman peaks and the reflections of unreacted phases of

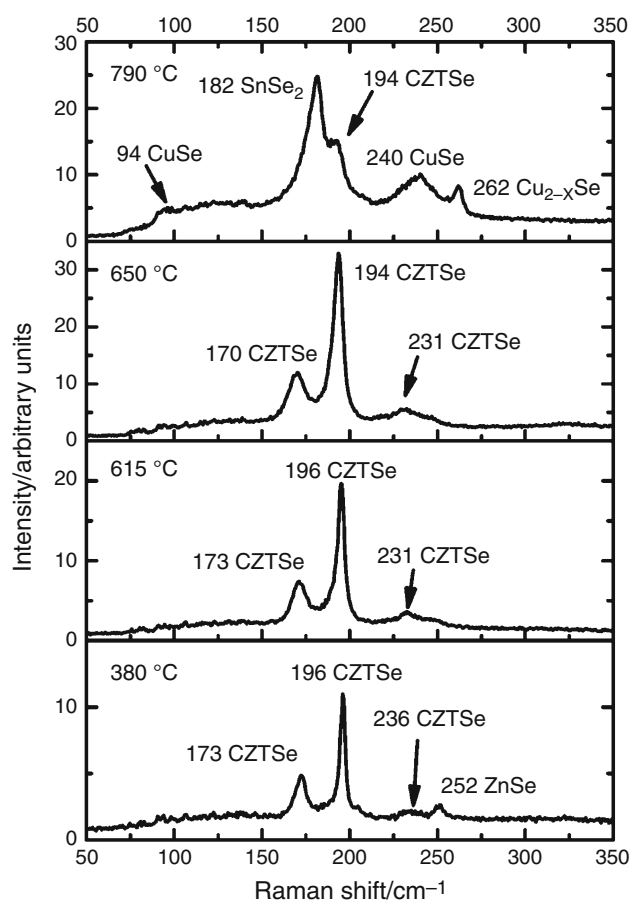


Fig. 5 Raman spectra of CuSe + ZnSe + SnSe + NaI mixtures quenched at different annealing temperatures (after washing out NaI and soluble phases with water)

ZnSe (in Raman spectra at 252 cm^{-1} [21]), $\text{Cu}_{1.8}\text{Se}$, CuSe, SnSe, and SnSe_2 are present in XRD patterns of samples heated at temperatures below the melting of NaI. In the sample heated at 650 °C , Raman can detect only single phase of CZTSe, while the XRD reflections are shifted in 2θ scale, which could occur due to some ternary $\text{Cu}_2\text{ZnSnSe}_3$ phase present. Sample, heated at 790 °C (over the highest incongruent melting point of CZTSe [24]) and quenched, shows again more binary compounds CuSe ($94, 240\text{ cm}^{-1}$ [5]), Cu_{2-x}Se (262 cm^{-1} [12]), SnSe, and SnSe_2 (182 cm^{-1} [15]) present. Due to the fast cooling after heating, the sample over the melting temperature of CZTSe the binaries do not reach to react with each other completely.

Conclusions

It can be concluded that in the presence of solid NaI the formation of CZTSe is inhibited. Chemical reactions start with the formation of a liquid phase in all of the mixtures studied. The melting of NaI is immediately followed by the extensive formation process of CZTSe starting already a

little bit below the melting point of NaI. The optimal temperature of synthesis of CZTSe in NaI is 650 °C . Dry and pure NaI allowing to reduce the synthesis temperature in comparison with KI can be successfully used as a flux material in synthesis of CZTSe in monograin powder form. On the basis of the results of Raman and the XRD analyses, it can be concluded that Se, released due to the decomposition of CuSe to $\text{Cu}_{1.8}\text{Se}$, reacts with SnSe forming SnSe_2 . However, CuSe does not decompose completely under the formed Se overpressure in the sealed ampoules. $\text{Cu}_2\text{ZnSnSe}_4$ formation starts partly already at 380 °C as a result of the reaction between Cu_2Se , ZnSe, and SnSe_2 . The main formation process of CZTSe is initiated by the formation of the molten phase of NaI in the precursor mixtures at temperatures a little bit lower than the melting point of pure NaI. The formation of $\text{Cu}_2\text{ZnSnSe}_4$ is completed in the formed molten phase of NaI. The occurrence of an intensive exothermic peak right after an endothermic peak due to the melting process in DTA curves suggests a strong chemical interaction between the precursors in the formed molten phase. The formation enthalpies of $\text{Cu}_2\text{ZnSnSe}_3$ in molten NaI starting from CuSe and SnSe $-32 \pm 3\text{ kJ mol}^{-1}$ at 655 °C and CZTSe from CuSe, SnSe, and ZnSe $-36 \pm 3\text{ kJ mol}^{-1}$ at 661 °C are experimentally determined for the first time.

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