Introduction to the Scientific Community – Inorganic Chemistry

Synthesis of ternary AgGaTe and CuGaSe compounds along binary lines

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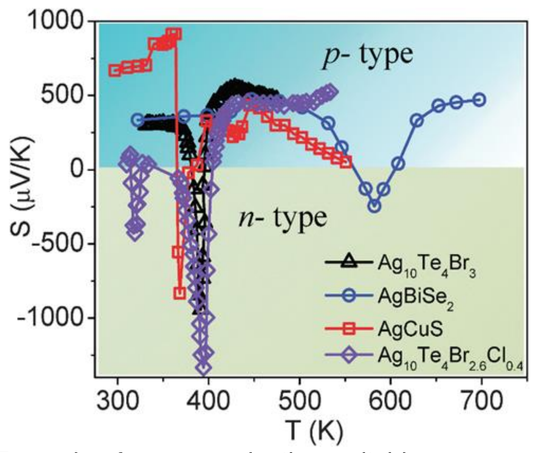
Introduction

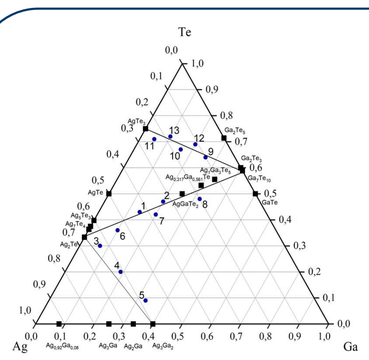
The high interest in tuning known or synthesizing new thermoelectric compounds with higher figure of merits led to a broad variation of thermoelectrica, such as p-n-p conduction switching materials. p-n-p switching semiconductors are a group of materials which undergo reversible switching from p- to n-type conduction due to applied changes in voltage or temperature. Responsible for this behavior are ion-mobility-driven order−disorder phase transitions with phonon softening effects leaving the composition of the material unchanged. This is usually coupled with band gap variations and changes in the density of states at the Fermi level, leading to an intermediate quasi-metallic state with increased valence electron conduction[1]. Therefore p-n-p conduction switching materials could be applicable in modern electronics such as in diodes, switches or transistor devices with functions depending on temperature changes near room temperature, or also voltage changes. Motivated by the applications, attempts were started to discover new semiconductors with p-n-p conduction switching behavior in both ternary systems AgGaTe and CuGaSe.



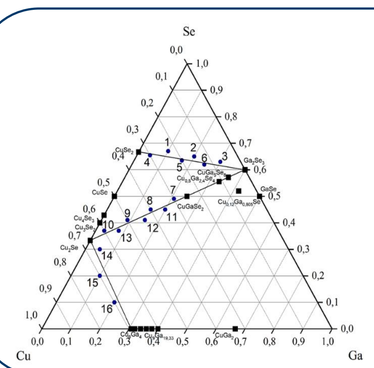
Example of p-n-p conduction switching behavior of already discovered compounds. Seebeck coefficient (*S*) *vs.* Temperature (*T*). Graphical content adapted form Lit. [1]

Method

Several compositions in both ternary phase diagrams were chosen along lines between two stable binary compounds.



Compositions along three binary lines of the AgGaTe ternary phase diagram



Compositions along three binary lines of the CuGaSe ternary phase diagram

Synthesis

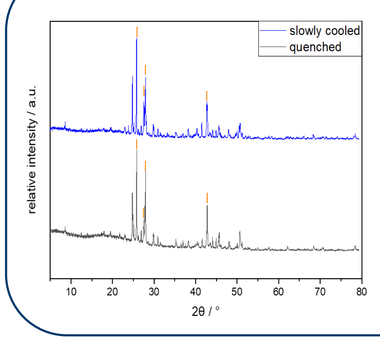
Reactions were conducted in vacuo via high temperature furnace synthesis. The products were synthesized via a thermodynamical approach, where heated to the highest melting point of the elemental compositions. Furthermore, every composition was both immediately and slowly cooled to see if varying the crystallization process has any impact on the phase formation.

Point	CuGaSe	AgGaTe
1	$Cu_{0.23}Ga_{0.1}Se_{0.67}$	$Ag_{0.43}Ga_{0.14}Te_{0.43}$
2	$Cu_{0.15}Ga_{0.2}Se_{0.65}$	$Ag_{0.33}Ga_{0.2}Te_{0.47}$
3	$Cu_{0.07}Ga_{0.3}Se_{0.63}$	$Ag_{0.63}Ga_{0.07}Te_{0.3}$
4	$Cu_{0.3}Ga_{0.045}Se_{0.655}$	$Ag_{0.61}Ga_{0.19}Te_{0.2}$
5	$Cu_{0.2}Ga_{0.165}Se_{0.635}$	$Ag_{0.58}Ga_{0.33}Te_{0.09}$
6	$Cu_{0.13}Ga_{0.25}Se_{0.62}$	$Ag_{0.54}Ga_{0.1}Te_{0.36}$
7	$Cu_{0.3}Ga_{0.21}Se_{0.49}$	$Ag_{0.38}Ga_{0.2}Te_{0.42}$
8	$Cu_{0.4}Ga_{0.15}Se_{0.45}$	$Ag_{0.2}Ga_{0.32}Te_{0.48}$
9	$Cu_{0.5}Ga_{0.09}Se_{0.41}$	$Ag_{0.1}Ga_{0.26}Te_{0.64}$
10	$Cu_{0.6}Ga_{0.03}Se_{0.37}$	$Ag_{0.17}Ga_{0.16}Te_{0.67}$
11	$Cu_{0.35}Ga_{0.2}Se_{0.45}$	$Ag_{0.24}Ga_{0.05}Te_{0.71}$
12	$Cu_{0.44}Ga_{0.15}Se_{0.41}$	$Ag_{0.11}Ga_{0.2}Te_{0.69}$
13	$Cu_{0.55}Ga_{0.08}Se_{0.37}$	$Ag_{0.18}Ga_{0.1}Te_{0.72}$
14	$Cu_{0.65}Ga_{0.05}Se_{0.3}$	-
15	$Cu_{0.7}Ga_{0.1}Se_{0.2}$	-
16	$Cu_{0.7}Ga_{0.2}Se_{0.1}$	-

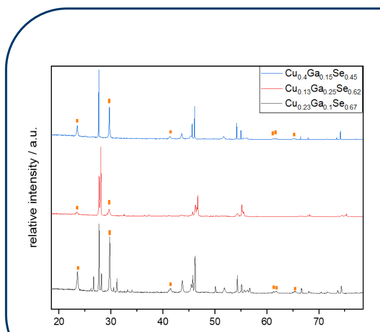
Different phase compositions of both ternary systems, which were used for reactions

Spectroscopy

Products were grounded and characterized by PXRD. Furthermore, the retrieved reflections were compared to spectra from the Pearson Crystal Database.



Reflections of slowly cooled and quenched $Ag_{0.1}Ga_{0.26}Te_{0.64}$ compared to each other. Orange markers display reflections which could not be identified.



Quenching of $Cu_{0.23}Ga_{0.1}Se_{0.67}$, $Cu_{0.13}Ga_{0.25}Se_{0.62}$ and $Cu_{0.4}Ga_{0.15}Se_{0.45}$ led also to unidentified reflections (orange)

Conclusion

Although some compositions within both systems led to the formation of products, which have shown unidentified reflections, a comparison to other databases must be performed. Yet most of the compositions have led to already known products. Therefore, a kinetic approach should be started, where more contact between the reactants is guaranteed, since the educts were only mixed heterogeneously in the previous experiments. The reactants must be e.g., finely ground with a ball mill to ensure a more homogeneous composition, which could possibly lead to formation of new phases.

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[1] S. N. Guin, K. Biswas, *Physical chemistry chemical physics : PCCP* **2015**, 17, 10316.