

Crystal structures of the four new quaternary copper(I)-selenides $A_{0.5}CuZrSe_3$ and $ACuYSe_3$ ($A = Sr, Ba$)

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Abstract

The four new quaternary copper(I)-selenides, $\text{Sr}_{0.5}\text{CuZrSe}_3$ ($a = 3.8386(7)$, $b = 14.197(2)$, $c = 10.1577(17)$ Å), $\text{Ba}_{0.5}\text{CuZrSe}_3$ ($a = 3.8386(7)$, $b = 14.196(2)$, $c = 10.1577(17)$ Å), SrCuYSe_3 ($a = 10.620(2)$, $b = 4.1000(8)$, $c = 13.540(3)$ Å) and BaCuYSe_3 ($a = 4.1800(7)$, $b = 13.940(2)$, $c = 10.6200(17)$ Å) were synthesized by high-temperature solid state reactions and their crystal structures were determined using single-crystal X-ray diffraction. $\text{A}_{0.5}\text{CuZrSe}_3$ ($A = \text{Sr}, \text{Ba}$) and BaCuYSe_3 crystallize in the KCuZrS_3 structure type ($Cmcm$), while SrCuYSe_3 is isostructural to Eu_2CuS_3 ($Pnma$). All compounds form layered structures in which the charge of the $\frac{2}{\infty}[\text{CuZrSe}_3]^-$ and $\frac{2}{\infty}[\text{CuYSe}_3]^{2-}$ layers as well as the site occupancy of the A cations depend on the transition metal. Combining the alkaline earth metals Sr and Ba with tetravalent Zr leads to the formation of cation vacancies between the $\frac{2}{\infty}[\text{CuZrSe}_3]^-$ layers and structure type as well as symmetry are determined by the ratio between the cation and transition metal ionic radii $r(A^{2+})/r(M^{3+/4+})$.

Introduction

Previous studies of transition metal chalcogenides, which contain open layers or channels unveiled interesting thermoelectric and magnetic properties.^[1-4] These open structural frameworks can be obtained by a charge transfer from strong cations such as Sr and Ba towards an anionic network containing transition metals and Se/Te. Copper chalcogenides are of particular interest due to the high Cu mobility, which can result in a “phonon-liquid-electron-crystal” type behavior, low heat capacities, structural disorder, fast ion conduction, superionicity and promising thermoelectric properties.^[5-11] Combining strong cations such as Ba with a Cu– Q network ($Q = \text{Se}, \text{Te}$) led towards a variety of new compounds with intriguing crystal structures containing Cu clusters and polychalcogen units such as hypervalent chains and square nets.^[12-15] The open, layered crystal structure of the ACuMQ_3 ($Q = \text{S}, \text{Se}, \text{Te}$; $M = \text{Zr}, \text{Hf}, \text{U}$ and lanthanides) family with its first member KCuZrQ_3 ^[16] has

a remarkable flexibility towards element substitution resulting in the same or a similar structure types with the group subgroup relationship *Cmcm-Pnma*.^[17] Up to now members of this family were obtained by combining di- (A^{2+}) and trivalent (M^{3+}) or mono- (A^+) and tetravalent (M^{4+}) cations with a $[\text{CuSe}_3]^{5-}$ network. Examples are combinations of alkaline earth and rare-earth metals (e.g. BaCuMSe_3 with $M = \text{La}^{[18]}$, $\text{Ce}^{[19]}$, $\text{Gd}^{[20]}$ and $\text{SrCuMSe}_3^{[21]}$ with $M = \text{La-Pr}$, Nd , Sm , Gd-Lu) or alkali and group 4 transition metals (e.g. $\text{KCuMSe}_3^{[16,22]}$, $\text{RbCuMSe}_3^{[22]}$, $\text{CsCuMSe}_3^{[20,22]}$ with $M = \text{Zr}$, Hf). For the SrCuMSe_3 ($M = \text{La}$, Gd , Lu)^[17] series the crystal structure changes between three orthorhombic structures with different coordination environments for Sr^{2+} and M^{3+} depending on the ionic radii of the lanthanides. The smaller Gd^{3+} for example is coordinated by six Se^{2-} ions, while the larger La^{3+} has a coordination number (CN) of seven. Going towards the even smaller Lu^{3+} does not change its CN, but Sr^{2+} gains another Se^{2-} ligand. The crystal structures of SrCuMSe_3 are higher symmetric (*Cmcm*) for the smaller and heavier lanthanides ($M = \text{Lu-Ho}$), while the symmetry is reduced for $M = \text{Dy-Gd}$, Sm , Nd-La resulting in the space group *Pnma*.^[17] Another example, where the M^{3+} cation radius changes the crystal structure is the study of $\text{SrCuCeSe}_3^{[23]}$ and $\text{SrCuPrSe}_3^{[23]}$, where the former crystallizes in its own structure type. The recent examples BaAgTbS_3 , BaCuGdTe_3 , BaCuTbTe_3 , BaAgTbTe_3 and CsAgUTe_3 as new members of the 1113 family underline the remarkable flexibility of the KCuZrS_3 structure type towards ion exchange.^[24] Here we report on the first members of the 1113 family with cation vacancies between the layers, which can be obtained by combining the alkaline-earth metals Ba/Sr with tetravalent Zr. Furthermore we demonstrate that not only the $M^{3+/4+}$ ($M = \text{Zr}$, Y) or A^{2+} ($A = \text{Ba}$, Sr) ionic radii determine structure type and symmetry, but their ratio $r(A^{2+})/r(M^{3+/4+})$. This conclusion also holds for the analogous SrCuMSe_3 ($M = \text{La}$, Ce , Pr , Gd , Lu) compounds^[17,23], which makes the $r(A^{2+})/r(M^{3+/4+})$ ratio a powerful parameter for predicting the symmetry of new compounds belonging to the “1113 family”.

Experimental

Synthesis

Single crystals of all title compounds were grown from conventional high-temperature solid state reactions. $\text{Ba}_{0.5}\text{CuZrSe}_3$ was synthesized from BaSe, Cu, Zr and Se precursors, SrCuYSe_3 from Cu_2Se , Sr, Y, Se and all other compounds were obtained from reactions of stoichiometric amounts of the elements. The BaSe precursor was synthesized by high-energy ball milling (700 rpm, 15 cycles of 2 min milling time using 10 mm tungsten carbide balls) from the elements. Cu_2Se was prepared by heating a stoichiometric mixture of the elements up to 600°C , where it was kept for 24 h and subsequently cooled down to room temperature in 24 h. All manipulations were carried out in an argon-filled glove box. Stoichiometric amounts of Cu shots (Alfa Aesar, 99.5 %) or Cu_2Se powder, Ba pieces (Alfa Aesar, 99+%) or BaSe powder, selenium shots (Alfa Aesar, 99.999%) and Zr sponge (Alfa Aesar, 99.5 %) or Y chips (Aldrich 99.9 %) were heated up in 7 h to 500°C in flame-sealed silica ampoules. The reaction temperature was kept constant for 24 h and subsequently raised to 800°C and kept constant for another 48 h before cooling the samples to 200°C within 96 h. Black needles with metallic luster were obtained for $A_{0.5}\text{CuZrSe}_3$ ($A = \text{Sr}, \text{Ba}$) and yellow needles for ACuYSe_3 ($A = \text{Sr}, \text{Ba}$). Attempts to obtain pure bulk samples for physical measurements failed due to unreacted Cu and Se as well as the presence of the stable binary side phases CuSe, Cu_2Se and ZrSe_3 .

Single crystal structure determination

All compounds are air-stable and therefore single crystals were picked in air under a thin film of oil. Intensity data was collected on a Bruker SMART diffractometer equipped with a SMART APEX II CCD area detector and a Mo- $K\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$) at a constant temperature of 293 K for $\text{Sr}_{0.5}\text{CuZrSe}_3$ and BaCuYSe_3 and 200 K for

Ba_{0.5}CuZrSe₃ and SrCuYSe₃. Data collections at 200 K were performed under a constant stream of nitrogen heated to the target temperature.

Data acquisition and processing were performed using the software SMART^[25] and APEX II, while data reduction and integration were performed using SAINT.^[26] Semiempirical absorption corrections were applied using SADABS.^[27] Structure solution and refinement were carried out using SHELX^[28] and Olex2^[29] was used as a Graphical User Interface for SHELX. The centrosymmetric, orthorhombic space groups *Pnma* for Sr_{0.5}CuYSe₃ and *Cmcm* for A_{0.5}CuZrSe₃ (A = Sr, Ba) and BaCuYSe₃ were established from the Laue symmetry, systematic absences and intensity statistics using the program XPREP and initial atomic positions were located by direct methods and the crystal structure data were standardized using the program STRUCTURE TIDY.^[30]

Important crystallographic information for all title compounds are provided in Table1. All final equivalent isotropic displacement factors and atomic coordinates are summarized in Table2, while Table3 gives an overview over selected interatomic distances in Sr_{0.5}CuZrSe₃, Ba_{0.5}CuZrSe₃, SrCuYSe₃ and BaCuYSe₃.

Crystal Structure Description and Discussion

Ba_{0.5}CuZrSe₃ and Sr_{0.5}CuZrSe₃ crystallize in the layered KCuZrS₃ structure type with the orthorhombic space group *Cmcm* ($a = 3.8386(7) \text{ \AA}$, $b = 14.197(2) \text{ \AA}$, $c = 10.1577(17) \text{ \AA}$ and $a = 3.8386(7) \text{ \AA}$, $b = 14.196(2) \text{ \AA}$, $c = 10.1577(17) \text{ \AA}$ respectively). The crystal structure (cf. Fig.1) consists of $\frac{2}{\infty}[\text{CuZrSe}_3]^-$ layers (cf. Fig.2) in the *ac* plane stacked along [010] and A²⁺ cations and vacancies, which are separating the anionic layers. The $\frac{2}{\infty}[\text{CuZrSe}_3]^-$ layers (cf. Fig.3) consist of an infinite $\frac{2}{\infty}[\text{ZrSe}_{2/2}\text{Se}_{4/2}]^{2-}$ network and $\frac{1}{\infty}[\text{CuSe}_{2/1}\text{Se}_{2/2}]^{5-}$ chains. The former is built up by ZrSe₆ octahedra, which share edges along [100] and vertices along [010] and the latter by vertex-sharing CuSe₄ tetrahedra. Two parallel $\frac{1}{\infty}[\text{CuSe}_{2/1}\text{Se}_{2/2}]^{5-}$ chains are rotated by 180° towards each other and the A²⁺ cations between the $\frac{2}{\infty}[\text{CuZrSe}_3]^-$ layers are

coordinated by 8 Se atoms forming a ASe_8 bicapped trigonal prism (*cf.* Fig.3), where A is either occupied by Sr/Ba or vacant.

$BaCuYSe_3$ ($a = 4.1800(7) \text{ \AA}$, $b = 13.940(2) \text{ \AA}$, $c = 10.6200(17) \text{ \AA}$) is isostructural to $KCuZrS_3$, while $SrCuYSe_3$ ($a = 10.620(2) \text{ \AA}$, $b = 4.1000(8) \text{ \AA}$, $c = 13.540(3) \text{ \AA}$) crystallizes in the Eu_2CuS_3 structure type ($Pnma$). The change in symmetry observed for $SrCuYSe_3$ does neither affect the building blocks in the ${}^2_\infty[CuMSe_3]$ layers described for the Zr compounds, nor their connectivity. Hence, the previous structural description for $Ba_{0.5}CuZrSe_3$ and $Sr_{0.5}CuZrSe_3$ (*cf.* Fig.1-3) can be used for both $ACuYSe_3$ ($A = Sr, Ba$) compounds. For $SrCuYSe_3$ the stacking direction of the layers changes from $[010]$ to $[001]$ and the ${}^1_\infty[CuSe_{2/1}Se_{2/2}]^{5-}$ chains run along $[010]$ instead of $[100]$.

Replacing tetravalent Zr by trivalent Y causes an increase in the negative charge of the ${}^2_\infty[CuMSe_3]$ layers from -1 to -2 and the cation position becomes fully occupied by Ba or Sr. Between the two compounds $Ba_{0.5}CuZrSe_3$ to $BaCuYSe_3$ the symmetry does not change despite the different ionic radii of Zr^{4+} (0.72 \AA)^[31] and Y^{3+} (0.90 \AA)^[31]. However, in the corresponding lanthanides the change of the M^{3+} ionic radius results in a different orthorhombic symmetry.^[17] Hence, only comparing the cation or the transition metal/lanthanum ionic radii is not sufficient to understand the change in symmetry upon element substitution. Comparing the ratio between the cation and transition metal/lanthanum ionic radii $r(A^{2+})/r(M^{3+/4+})$ on the other hand clearly shows, that the higher symmetric $KCuZrS_3$ structure type ($Cmcm$) forms for $r(A^{2+})/r(M^{3+/4+}) > 1.32$, while the lower symmetric space group $Pnma$ adopted for example by the Eu_2CuS_3 and $PbCuLaS_3$ structure types is favored for $r(A^{2+})/r(M^{3+/4+}) < 1.41$ (*cf.* Fig.4). Hence, the threshold for a change from the higher symmetric space group $Cmcm$ to the lower symmetric subgroup $Pnma$ lies in between these two values. The difference in symmetry observed for $SrCuYSe_3$, which is accompanied by a change in the local coordination environment of the A^{2+} cation from a bicapped trigonal

BaSe₈ prism to a monocapped trigonal SrSe₇ prism can therefore be explained by its $r(\text{Sr}^{2+})/r(\text{Y}^{3+})$ ratio of 1.32 – the lowest for the four title compounds. Hence, Yttrium represents the frontier between transition metal and lanthanide chemistry in the “1113 family”.

Replacing tetravalent Zr by trivalent Y also leads to an increase in unit cell volume (cf. Fig.5) from 553 Å³ to 619 Å³ going from Ba_{0.5}CuZrSe₃ to BaCuYSe₃ due to a larger ionic radius of Y³⁺ (0.90 Å)^[31] compared to Zr⁴⁺ (0.72 Å)^[31]. The larger cell volume is a net result of a simultaneous increase in all intralayer transition metal distances and a decrease in the interlayer distances (cf. Fig.6-7) causing *a* and *c* to enlarge and *b* to contract (cf. Fig.5). Replacing the larger Ba²⁺ (ionic radius: 1.42 Å for CN = 8)^[31] by the smaller Sr²⁺ (ionic radii: 1.26 Å for CN = 7 and 1.21 Å for CN = 7)^[31] in ACuYSe₃ decreases the unit cell volume (cf. Fig.5) from 619 Å³ for BaCuYSe₃ to 590 Å³ for SrCuYSe₃, which is mainly caused by shorter interlayer distances (visualized as A²⁺ ••• A²⁺ distances in Fig.6) in SrCuYSe₃ compared to BaCuYSe₃. Fig.8 shows the range of the cation-selenium distances of all four title compounds. The A-Se distances are significantly larger in BaCuYSe₃ compared to SrCuYSe₃ due to the different ionic radii of Ba²⁺ and Sr²⁺, which explains the shorter interlayer distances in SrCuYSe₃ compared to BaCuYSe₃ and the difference in unit cell volume.

The maximum cation-selenium distances (cf. Fig. 8) increase with a decreasing $r(\text{A}^{2+})/r(\text{M}^{3+/4+})$ ratio (cf. Fig.4 and Fig.8) and the distortion around the CuSe₄ and MSe₆ polyhedra is largest for BaCuYSe₃ with a $r(\text{A}^{2+})/r(\text{M}^{3+/4+})$ ratio closest to the critical one before the *Cmcm-Pnma* transition. Hence, it is probable that too long cation-selenium distances in combination with a certain degree of structural distortion around the CuSe₄ and MSe₆ polyhedra trigger the change in A²⁺ coordination number and symmetry, which is accompanied by a reduction in structure distortion and maximum cation-selenium distances (cf. Fig.8).

Conclusion

The four new quaternary copper(I)-selenides, $\text{Sr}_{0.5}\text{CuZrSe}_3$, $\text{Ba}_{0.5}\text{CuZrSe}_3$, SrCuYSe_3 and BaCuYSe_3 were synthesized by high-temperature solid state reactions and their crystal structures were determined using single-crystal X-ray diffraction. A combination of the alkaline-earth metals Ba and Sr with the group 4 transition metal Zr leads to a stabilization of the KCuZrS_3 structure type accompanied by the formation of cation vacancies. Replacing tetravalent Zr by trivalent Y causes an increase in the negative charge of the ${}^2_{\infty}[\text{CuMSe}_3]$ layers from -1 to -2 and the cation position is fully occupied by Ba or Sr. $\text{Ba}_{0.5}\text{CuZrSe}_3$, $\text{Sr}_{0.5}\text{CuZrSe}_3$ and BaCuYSe_3 crystallize in the higher symmetric KCuZrS_3 structure type ($Cmcm$), while SrCuYSe_3 is isostructural to Eu_2CuS_3 crystallizing in the orthorhombic space group $Pnma$ - a subgroup of $Cmcm$. The cation coordination environment in BaCuYSe_3 and SrCuYSe_3 changes from a bicapped trigonal BaSe_8 prism towards a monocapped trigonal SrSe_7 prism, the ${}^2_{\infty}[\text{CuMSe}_3]$ layers are stacked along $[001]$ instead of $[010]$ and the ${}^1_{\infty}[\text{CuSe}_{2/1}\text{Se}_{2/2}]^{5-}$ chains run along $[010]$ instead of $[100]$. The ratio between the cation and transition metal ionic radii $r(A^{2+})/r(M^{3+/4+})$ determines symmetry and structure type, which does not only apply to the four title compounds, but also to the previously reported SrCuMSe_3 ($M = \text{La, Gd, Lu}$) family and it can even be extended to SrCuPrSe_3 and SrCuCeSe_3 . Compounds with $r(A^{2+})/r(M^{3+/4+}) > 1.32$ crystallize in the higher symmetric KCuZrS_3 structure, while the lower symmetric Eu_2CuS_3 and PbCuLaS_3 structure types ($Pnma$) are favored for $r(A^{2+})/r(M^{3+/4+}) < 1.41$. A transition from the higher to the lower symmetric space group occurs between these two values, which explains the lower symmetry observed for SrCuMSe_3 ($M = \text{La, Gd, Lu, Ce, Pr}$) and SrCuYSe_3 . The $r(A^{2+})/r(M^{3+/4+})$ ratio can therefore

be used as a very intuitive and powerful parameter to explain and predict structure type and symmetry for compounds belonging to the 1113 family.

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Table 1

General crystallographic information obtained from single crystal structure solutions and refinements.

	Ba_{0.5}CuZrSe₃	Sr_{0.5}CuZrSe₃	BaCuYSe₃	SrCuYSe₃
Formula weight (amu)	460.31	435.46	526.67	477.95
Space group	<i>Cmcm</i> (No. 63)	<i>Cmcm</i> (No. 63)	<i>Cmcm</i> (No. 63)	<i>Pnma</i> (No. 62)
<i>a</i> (Å)	3.8386(7)	3.8386(7)	4.1800(7)	10.620(2)
<i>b</i> (Å)	14.196(2)	14.197(2)	13.940(2)	4.1000(8)
<i>c</i> (Å)	10.1577(17)	10.1577(17)	10.6200(17)	13.540(3)
<i>V</i> (Å ³)	553.54(17)	553.54(17)	618.82(18)	589.6(2)
<i>Z</i>	4	4	4	4
F(000)	796	746	904	816
ρ_{calcd} (g cm ⁻³)	5.523	5.2499	5.653	5.373
<i>T</i> (K)	200(2)	293(2)	293(2)	200(2)
Crystal dimensions (mm)	0.270×0.043×0.033	0.323×0.060×0.071	0.151×0.097×0.087	0.192×0.073×0.049
Radiation	Mo <i>K</i> α, $\lambda = 0.71073$ Å			
μ (Mo <i>K</i> α) (mm ⁻¹)	28.764	30.272	36.495	40.823
2 θ limits	5.74 - 61.38	5.74 - 55.08	5.74 - 68.37	4.88 - 60.08
Data collected	-5≤ <i>h</i> ≤ 5, -20≤ <i>k</i> ≤ 20, -14≤ <i>l</i> ≤ 14	-4≤ <i>h</i> ≤ 4, -17≤ <i>k</i> ≤ 17, -13≤ <i>l</i> ≤ 12	-6≤ <i>h</i> ≤ 3, -17≤ <i>k</i> ≤ 22, -12≤ <i>l</i> ≤ 16	-13≤ <i>h</i> ≤ 14, -5≤ <i>k</i> ≤ 5, -19≤ <i>l</i> ≤ 18
No. of measured reflections	4403	2807	2277	5048/
No. of unique reflections with <i>I</i> > 2σ(<i>I</i>)	512	363	636	972
No. of parameters	23	22	23	36
<i>R</i> (<i>F</i>) for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0257	0.0237	0.0281	0.0331
<i>R</i> _w (F_o^2) ^b / <i>R</i> _{int}	0.0675/0.0271	0.0610/0.0324	0.0674/0.0478	0.0761/0.0536
Goodness of fit	1.185	1.025	1.274	0.982
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	1.373, -1.074	1.3973, -0.6595	2.046, -2.891	1.7234, -1.9452

Table 2Equivalent isotropic displacement factors (\AA^2)^a and positional parameters.

Atom	Wyckoff position	s.o.f.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2) ^a
Ba_{0.5}CuZrSe₃						
Ba1	4 <i>c</i>	0.5	0	0.74576(6)	0.25	0.0133(2)
Zr1	4 <i>a</i>	1	0	0	0	0.01254(19)
Cu1	4 <i>c</i>	1	0	0.46230(8)	0.25	0.0179(2)
Se1	8 <i>f</i>	1	0	0.37049(4)	0.05046(5)	0.01142(16)
Se2	4 <i>c</i>	1	0	0.06851(6)	0.25	0.01275(19)
Sr_{0.5}CuZrSe₃						
Sr1	4 <i>c</i>	0.5	0	0.74890(12)	0.25	0.0145(4)
Zr1	4 <i>a</i>	1	0	0	0	0.0122(2)
Cu1	4 <i>c</i>	1	0	0.46467(9)	0.25	0.0185(3)
Se1	8 <i>f</i>	1	0	0.36517(4)	0.05322(6)	0.0112(2)
Se2	4 <i>c</i>	1	0	0.07555(6)	0.25	0.0119(2)
BaCuYSe₃						
Ba1	4 <i>c</i>	1	0	0.74671(4)	0.2500	0.0112(2)
Y1	4 <i>a</i>	1	0	0	0	0.0077(3)
Cu1	4 <i>c</i>	1	0	0.46711(10)	0.25	0.0142(4)
Se1	8 <i>f</i>	1	0	0.36482(5)	0.05983(6)	0.0082(2)
Se2	4 <i>c</i>	1	0	0.06907(7)	0.25	0.0075(3)
SrCuYSe₃						
Sr1	4 <i>c</i>	1	0.26253(7)	0.25	0.00078(6)	0.01287(19)
Y1	4 <i>c</i>	1	0.00916(6)	0.25	0.24641(5)	0.00862(19)

Cu1	4c	1	0.24284(8)	0.25	0.72144(8)	0.0135(2)
Se1	4c	1	0.055497)	0.25	0.61281(5)	0.00953(19)
Se2	4c	1	0.25741(6)	0.25	0.32879(6)	0.00871(19)
Se3	4c	1	0.42449(7)	0.25	0.60816(5)	0.00964(19)

Table 3

Selected interatomic distances

Atom pairs	Distances (Å).	Atom pairs	Distances (Å).
Ba_{0.5}CuZrSe₃			
Ba1•••Ba1	3.8386(7)	Zr1•••Se1 (4x)	2.7068(5)
Se1 (4x)	3.3057(7)	Se2 (2x)	2.7193(5)
Se1 (2x)	3.4696(9)	Cu1•••Se1 (2x)	2.4098(9)
Se2 (2x)	3.1647(11)	Se2 (2x)	2.4407(9)
Zr1•••Cu1 (4x)	3.2278(4)		
Sr_{0.5}CuZrSe₃			
Sr1•••Sr1	3.8386(7)	Zr1•••Se1 (4x)	2.7640(5)
Se1 (4x)	3.2254(10)	Se2 (2x)	2.7566(5)
Se1 (2x)	3.4798(11)	Cu1•••Se1 (2x)	2.4476(10)
Se2 (2x)	3.1210(16)	Se2 (2x)	2.4823(10)
Zr1•••Cu1 (4x)	3.2224(4)		
BaCuYSe₃			
Ba1•••Ba1	4.1800(7)	Y1•••Se1 (4x)	2.8849(6)
Se1 (4x)	3.3404(7)	Se2 (2x)	2.8242(5)
Se1 (2x)	3.6392(9)	Cu1•••Se1 (2x)	2.4723(11)
Se2 (2x)	3.2404(10)	Se2 (2x)	2.5275(10)
Y1•••Cu1 (4x)	3.4099(4)		
SrCuYSe₃			
Sr1•••Sr1	4.1000(8)	Y1•••Se1 (2x)	2.8641(8)
Se1 (2x)	3.2033(9)	Se2 (2x)	2.8628(10)
Se2 (2x)	3.1096(9)	Se3 (2x)	2.8822(8)
Se3	3.4705(12)	Cu1•••Se1 (2x)	2.4646(12)
Se3 (2x)	3.1998(9)	Se2	2.5130(8)
		Se3	2.4742(12)

Fig. 1 Crystal structure of $A_{0.5}CuZrSe_3$ ($A = Sr, Ba$). ${}^2_{\infty}[CuZrSe_3]^-$ layers in the ac -plane are separated by A^{2+} cations and stacked along b . red: A; white: vacancies, blue: Cu, dark green: Zr, light green: Se.

Fig. 2 The ${}^2_{\infty}[CuZrSe_3]^-$ layer, which is built up by one dimensional chains of corner-sharing $CuSe_4$ tetrahedra running along a and the two dimensional network of $ZrSe_6$ octahedra sharing edges along a and corners along c . Two separated ${}^1_{\infty}[CuSe_{2/1}Se_{2/2}]^{5-}$ chains are rotated by 180° .

Fig. 3 a) linear ${}^1_{\infty}[CuSe_{2/1}Se_{2/2}]^{5-}$ chains built up by corner sharing $CuSe_4$ tetrahedra; b) edge- and corner sharing $ZrSe_6$ octahedra forming an infinite two dimensional Zr-Se network. The same building blocks and connectivity can be found in the ${}^2_{\infty}[CuYSe_3]^{2-}$ layers with YSe_6 octahedra; c) $A_{0.5}Se_8$ bicapped trigonal prism in $A_{0.5}CuZrSe_3$ ($A = Sr, Ba$).

Fig. 4 Ratio between the cation and transition metal/lanthanum ionic radii $r(A^{2+})/r(M^{3+/4+})$. Black squares: the four title compounds containing transition metals; blue squares: $SrMCuSe_3$ compounds with $M = Lu, Gd, Pr, Ce, La$. The image shows the symmetry dependence on the $r(A^{2+})/r(M^{3+/4+})$ ratio with a change from the higher symmetric space group $Cmcm$ to the lower symmetric space group $Pnma$ between $1.41 < r(A^{2+})/r(M^{3+/4+}) < 1.32$. All ionic radii were taken from [31].

Fig. 5 Changes in the lattice parameters and unit cell volume depending on the transition metal and the cation in the structure. The first letters on the y axis correspond to the lattice parameters and unit cell volume of the compounds crystallizing in the higher symmetric $Cmcm$ space group ($Ba_{0.5}CuZrSe_3$ and $BaCuYSe_3$), while the second ones correspond to $SrCuYSe_3$ crystallizing in the lower symmetric space group $Pnma$. Changing from Zr^{4+} (ionic radius: 0.72 \AA) to Y^{3+} (ionic radius: 0.90 \AA) results in a larger unit cell volume due to a simultaneous decrease in b and increase in a and c . Changing the cation from Ba^{2+} (ionic radius: 1.42 \AA) to Sr^{2+} (ionic radius: 1.21 \AA for CN = 7) in $ACuYSe_3$ decreases the unit cell volume due to a simultaneous decrease in the stacking direction of the ${}^2_{\infty}[CuYSe_3]^{2-}$ layers and the direction along the ${}^1_{\infty}[CuSe_{2/1}Se_{2/2}]^{5-}$ chains.

Fig. 6 Differences in the $A^{2+} \cdots A^{2+}$ interatomic distances (representing the intra- and interlayer distances) between $Ba_{0.5}CuZrSe_3$, $BaCuYSe_3$ and $SrCuYSe_3$. Black, blue and red arrows mark the corresponding distances in the structure (red: Ba, Sr; white: vacancies in the case of $Ba_{0.5}CuZrSe_3$; light green: Se, dark green: Zr/Y, blue: Cu). Changing the transition

metal from Zr^{4+} (ionic radius: 0.72 Å) to Y^{3+} (ionic radius: 0.90 Å) results in a simultaneous increase/decrease in the intra-/interlayer cation distances causing the increase in a and c going from $Ba_{0.5}CuZrSe_3$ to $BaCuYSe_3$ due to the larger ionic radius of Y^{3+} . Changing the cation from Ba^{2+} (ionic radius: 1.42 Å) to Sr^{2+} (ionic radius: 1.26 Å for CN = 8 and 1.21 Å for CN = 7) in $ACuYSe_3$ decreases the interlayer cation distances, which causes the decrease in the lattice parameters along the stacking direction of the ${}^2_{\infty}[CuYSe_3]^{2-}$ layers.

Fig. 7 Differences in the intralayer transition metal distances between $Ba_{0.5}CuZrSe_3$, $BaCuYSe_3$ and $SrCuYSe_3$. Orange, blue and red arrows mark the corresponding distances in the ${}^2_{\infty}[CuZrSe_3]^-$ and ${}^2_{\infty}[CuYSe_3]^{2-}$ layers (light green: Se, dark green: Zr/Y, blue: Cu). Changes in these layers are much more pronounced for a change in the transition metal compared to a change in the cation. The simultaneous increase of all intralayer transition metal distances upon a change from the smaller Zr^{4+} (ionic radius: 0.72 Å) to the larger Y^{3+} (ionic radius: 0.90 Å) causes the observed increase in a , c and the unit cell volume going from $Ba_{0.5}CuZrSe_3$ to $BaCuYSe_3$. The decrease in the intralayer transition metal distances for the direction along the ${}^1_{\infty}[CuSe_{2/1}Se_{2/2}]^{5-}$ chains corresponds to the decrease in the lattice parameter from $BaCuYSe_3$ to $SrCuYSe_3$ in this direction.

Fig. 8 Red: $A\cdots Se$ ($A = Sr, Ba$), blue: $Cu\cdots Se$ and green: $M\cdots Se$ ($M = Zr, Y$) distance ranges in the four title compounds (1: $Ba_{0.5}CuZrSe_3$, 2: $Sr_{0.5}CuZrSe_3$, 3: $BaCuYSe_3$, 4: $SrCuYSe_3$). The largest distortion in the $CuSe_4$ tetrahedra and MSe_6 octahedra is present for $BaCuYSe_3$ with a $r(A^{2+})/r(M^{3+/4+})$ ratio closest to the critical one and an increase in the maximum cation-selenium distances with a decreasing $r(A^{2+})/r(M^{3+/4+})$ ratio was found for the three higher symmetric title compounds.







