Electronic supplementary information:

Experimental:

1. UV/Vis spectroscopy

The measurement was taken using a Shimadzu 2700 UV/Vis spectrophotometer equipped with a UV/Vis DiffuseIR cell (Pike Technologies). Barium sulphate was used for baseline correction. Data were collected in a wavelength range of 200 - 900 nm.

In accordance with the Tauc's method [1, 2], the band gap energy for all the samples were estimated by finding the intercept of the abscissa from the following relations.

$$F(R)(h\nu) = A(h\nu - E_g)^{1/n}$$

where R is the reflectance, h is the Planck's constant, ν the frequency of light, E_g the band gap in eV and n depends on the type of optical transition, it could be $n = 2$ and/or 1/2 refers to indirect and direct transition, respectively. Recently, a new method "the derivation of absorption spectrum fitting (DASF)" [3] was suggested to calculate the band gap energies without considering any type of transition. Based on the following equation, this method was used as well for polycrystalline material:

$$\frac{dInF(R)}{\mathrm{d}h\nu} = \frac{n}{h\nu - Eg}$$

Herein, the transition type and the width of the band gap energy were determining based on a combination of the Reflectance-Absorption-Tauc-DASF (RATD) method [4].

The equation $\frac{dInF(R)}{\mathrm{d}h\nu} = \frac{n}{h\nu - Eg}$ helps to calculate the absolute value of band-gap energy E_g, which could be expressed by: $Eg = \frac{hc}{\lambda_g} = \frac{1239.81}{\lambda_g}\ [eV]$ [4]. The idea is to get rid of the fixed transition exponent "n" by calculating the derivative of the absorption spectrum [4]. To its original successful use with thin films, this method was recently utilized for powders to determine the band gap energy. The experimental work described herein demonstrates the possibility of employing the Reflectance-Absorption-Tauc-DASF (RATD) method, for deriving the transition types and band-gap energies of a series of isostructural compounds with varying composition [4 and 42 (see main article references)].

2. Scanning electron microscopy

Initially, to increase the conductivity of the samples, they were placed on conductive carbon tabs (fixed on an aluminum stub) and deposited with gold for 20 s using JFC-1200 (JEOL) coating followed by insertion into the SEM chamber. After that, the morphology, grain size distribution and homogeneity of the prepared powders were examined with a JMS-6510 (JEOL) equipped with an X-Flash 410-M detector (Bruker) for energy dispersive X-ray spectroscopy.

3. Thermo-gravimetric analysis (TGA)

Thermal stability of this series of double perovskite were measured by thermo-gravimetric analysis (TGA) coupled with Differential Scanning Calorimetry (DSC) using TGA/DSC 3+ STARe System of Mettler Toledo. The samples were measured with a heating rate of 10 K/min and a continuous N_2 flow of 20 mL/min from 300 to 1273 K. The compounds amounts are 19.8(1) mg, 21.1(1) mg, 19.87(1) mg, 20.5(1) mg, and 20.9(1) mg for *x = 0, 0.25, 0.5, 0.75* and *1*, respectively, which were measured relative to an empty corundum reference crucible.

References:

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[2]. Tauc J, Grigorovici R, Vancu A (1966) Optical Properties and Electronic Structure of Amorphous Germanium. *Phys Status Solidi B* 15:627–637. doi.org/10.1002/pssb.19660150224

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[4]. Ghosh K, Murshed MM, Fischer M, Gesing TM (2022) Aluminum to germanium inversion in mullite-type $RAlGeO_5$: Characterization of a rare phenomenon for R = Y, Sm–Lu. *J. Am. Ceram. Soc.*, 105(1): 728-741. doi.org/10.1111/jace.18085