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## High Temperature Transport Properties of Colusite $\text{Cu}_{24}\text{T}_2\text{V}_2\text{Ge}_6\text{S}_{32}$ ( $\text{T} = \text{Ni}, \text{Co}$ )

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### ABSTRACT

Sulfur-based minerals have emerged as interesting candidates for thermoelectric applications at high temperatures, tetrahedrites and colusites being two prominent examples. Herein, we extend the investigations on the latter family by reporting on the synthesis and the high-temperature thermoelectric properties of two polycrystalline colusites  $\text{Cu}_{24}\text{Ni}_2\text{V}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{24}\text{Co}_2\text{V}_2\text{Ge}_6\text{S}_{32}$ . Both samples were prepared by powder metallurgy and consolidated by spark plasma sintering (SPS). Successful substitution of Ni and Co for Cu was confirmed by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM) that further revealed a homogeneous distribution of the elements within the colusite matrix. The electrical resistivity and thermopower values measured in the Ni sample indicate a more pronounced metallic character with respect to the Co sample. These two samples exhibit very low lattice thermal conductivities of the order of  $0.5 \text{ W m}^{-1} \text{ K}^{-1}$  at 690 K. Despite this remarkable property, the Ni and Co concentrations studied herein did not give rise to enhanced  $ZT$  values relative to the previously reported parent compound  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  with a peak  $ZT$  value of 0.5 at 690 K achieved in the Ni sample.

## INTRODUCTION

Sulfur-based minerals are often composed of relatively inexpensive and Earth-abundant elements and show a rich chemistry. Some of them feature semiconducting electronic properties combined with a poor ability to transport heat, making them a fertile playground to design novel efficient thermoelectric materials [1-4]. Their potential for thermoelectric applications is assessed through the dimensionless thermoelectric figure of merit  $ZT$  defined as  $ZT = \alpha^2 T / \rho \kappa$  where  $T$  is the absolute temperature,  $\alpha$  is the thermopower or Seebeck coefficient,  $\rho$  is the electrical resistivity and  $\kappa$  is the total thermal conductivity [5-7].

Tetrahedrites based on  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  are prominent examples of naturally-occurring compounds in which good thermoelectric performances can be achieved with  $ZT$  values reaching unity around 700 K [8-19]. In addition to this family, colusites also show interesting transport properties [20-23]. They possess a general chemical formula  $\text{Cu}_{26}\text{V}_2\text{M}_6\text{S}_{32}$  ( $M = \text{As}, \text{Sn}, \text{Ge}, \text{Sb}$ ) and crystallize in the cubic space group  $P\bar{4}3n$  [24,25]. The crystal structure (Figure 1) can be viewed as a three-dimensional network of  $\text{VS}_4$  tetrahedra that share six edges with  $\text{CuS}_4$  tetrahedra themselves sharing corners with  $\text{MS}_4$  tetrahedra. Regardless of the composition, colusites show  $p$ -type electrical conduction with large thermopower values that exceed  $200 \mu\text{V K}^{-1}$  above 300 K [20-22]. The large and complex unit cell (66 atoms) leads to very low lattice thermal conductivity values at high temperatures ( $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ ) [20-23]. Likewise in tetrahedrites, several transition metals such as Zn or Fe can substitute for Cu thereby offering the possibility to optimize the thermoelectric performances by adjusting the hole concentration [20,21]. In addition, off-stoichiometry on the Cu or Sn site provides another tuning parameter of the hole concentration [21]. The beneficial combination of these properties results in maximum  $ZT$  values of 0.73 and 0.56 at 663 K for  $M = \text{Ge}$  and Sn,

respectively [22]. Despite these encouraging results, only few studies have been devoted so far to this family of compounds.

Because in tetrahedrites partial substitutions of Ni and Co for Cu significantly improve the thermoelectric properties [11,12,15], we tried to determine whether these elements influence similarly the transport in colusites. Herein, we report on the synthesis, crystal structure and high-temperature thermoelectric properties of two polycrystalline Ge-containing colusites with chemical compositions  $\text{Cu}_{24}\text{Ni}_2\text{V}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{24}\text{Co}_2\text{V}_2\text{Ge}_6\text{S}_{32}$ . Our structural and chemical characterizations confirmed the successful insertion of Ni and Co into the crystal structure. Unlike tetrahedrites, we find that the presence of Ni and Co does not give rise to higher  $ZT$  values with respect to the parent compound  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$ . Maximum  $ZT$  values of 0.4 and 0.5 at 690 K were obtained in the Co- and Ni-containing samples, respectively.

## EXPERIMENTAL DETAILS

Polycrystalline colusites  $\text{Cu}_{24}\text{Ni}_2\text{V}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{24}\text{Co}_2\text{V}_2\text{Ge}_6\text{S}_{32}$  were synthesized by weighting stoichiometric amounts of high-purity elements that were subsequently introduced into evacuated quartz tubes. The tubes were sealed under secondary vacuum, placed in a vertical oscillating furnace and heated slowly up to 1373 K. The tubes were dwelt at this temperature for 50 h and then furnace-cooled to room temperature. The obtained ingots were ground into fine powders, which were consolidated by spark plasma sintering (SPS) in a graphite die under pressure of 50 MPa at 1073 K for 15 min. The relative densities of the Ni and Co samples, estimated from weight and geometrical dimensions, were found to be 94 and 96%, respectively, of the theoretical density.

Powder X-ray diffraction (PXRD) data were collected by using a Bruker D8 Advance diffractometer (CuK $\alpha_1$  radiation,  $\lambda = 1.54056$  Å). The PXRD data were refined by the Rietveld method using the Fullprof software to determine the lattice parameter. The chemical homogeneity of the samples was assessed by scanning electron microscopy (SEM) using a Quanta 650 FEG (FEI). Surface images were collected in the backscattered electron mode (BSE) to contrast the colusite phase from impurity phases. The spatial distribution of the elements was determined by X-ray elemental mapping.

Electrical resistivity and thermopower were measured with a ZEM-3 system (Ulvac-Riko) in the temperature range 300 – 700K. The thermal conductivity was determined in the same temperature range by measuring the thermal diffusivity  $d$  by a laser flash technique (LFA 427, Netzsch). The thermal conductivity was then calculated from  $\kappa = dC_p\alpha_V$  where  $C_p$  is the isobaric specific heat and  $\alpha_V$  is the experimental density of the sample. As a first approximation, the specific heat was calculated by the Dulong-Petit law and hence, was considered temperature-independent. The temperature dependence of the density was neglected. The overall experimental uncertainty in the  $ZT$  values is estimated to be 17% [26].

## RESULTS AND DISCUSSION

### Structural and chemical characterizations

Figures 2a and 2b show the Rietveld refinements of the PXRD patterns of the Co and Ni samples, respectively, based on the structural model reported for colusite. The results indicate that some impurity phases are present in addition to the main colusite phase. Consistent with the results obtained by Suekuni *et al.* [20-22], the reflections corresponding to the colusite phase for both samples are not split. This contrasts with the Sn-containing analogue where

two colusite phases with slightly different composition coexist [20-22], a situation similar to the exsolution process seen in tetrahedrites [27-29]. The lattice parameters  $a$  inferred from these refinements are 10.5811(3) and 10.6292(4) Å for the Ni and Co samples, respectively. Both values are higher than that of the parent compound  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  (10.576(6) Å, [20]) evidencing the successful insertion of Ni and Co into the crystal structure.

SEM analyses (Figure 3) confirm the presence of Ni and Co within the colusite matrix and reveal a homogeneous distribution of all elements. These experiments further show that small amounts of  $\text{Cu}_2\text{S}$  and  $\text{NiS}_2$  are present as impurity phases in the Ni sample. In the Co sample,  $\text{Cu}_8\text{GeS}_6$  and pure vanadium are both present in small quantities besides the main colusite phase. EDXS analyses tend to indicate that the Ni concentration is lower than the nominal content while the Co concentration is very close to that expected.

## Transport Properties

Figures 4a and 4b show the temperature dependence of the electrical resistivity and thermopower of the Ni and Co samples. The Co sample exhibits high  $\rho$  and  $\alpha$  values at 300 K. Upon heating,  $\rho$  slightly decreases up to 450 K before increasing at higher temperatures possibly due to changes in the charge carrier mobility and scattering mechanisms. The positive  $\alpha$  values, indicative of hole-dominated transport, increases with increasing temperature to reach 265  $\mu\text{V K}^{-1}$  at 690 K. In contrast, the Ni sample shows a more pronounced metallic character, with significantly lower  $\rho$  and  $\alpha$  values that equal 35  $\mu\Omega \text{ m}$  and 145  $\mu\text{V K}^{-1}$  at 690 K. Compared to the unsubstituted compound  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  [22], the partial substitution of Co for Cu yields higher  $\rho$  and  $\alpha$  values in the whole temperature range while Ni gives rise to the opposite trend. The behavior observed in the Co sample is consistent with the results obtained in the  $\text{Cu}_{26-x}\text{Zn}_x\text{V}_2\text{M}_6\text{S}_{32}$  ( $M = \text{Ge}$  and  $\text{Sn}$ ) series where the

transport gradually evolves from metallic ( $x = 0$ ) towards semiconducting ( $x = 4$ ) regardless of the nature of the  $M$  atoms [20]. This trend suggests that Co provides additional electrons as observed in tetrahedrites for which substituting transition metals for Cu decreases the hole concentration and concomitantly increases  $\rho$  and  $\alpha$  [8-19]. The opposite behavior observed in the Ni sample suggests a more complicated situation than expected by simple electron counting rules that might be linked to a non-rigid-like evolution of the electronic band structure.

Figure 5a displays the total thermal conductivity as a function of temperature. For both specimen,  $\kappa$  decreases monotonically with increasing temperature to reach 0.8 and 0.55 W m<sup>-1</sup> K<sup>-1</sup> at 690 K in the Ni and Co sample, respectively. The difference observed between the two sets of data stems from the electronic contribution, which is significantly higher in the Ni sample due to its metallic character. This contribution has been estimated by using the Wiedemann-Franz law  $\kappa_e = LT/\rho$  where  $L$  is the Lorenz number. As a first approximation, we used the degenerate limit of  $L$  *i.e.*  $L = L_0 = 2.45 \cdot 10^{-8} \text{ V}^2 \text{ K}^{-2}$  to estimate  $\kappa_e$ . The results (Figure 5b) indicate that both samples show extremely low  $\kappa_L = \kappa - \kappa_e$  values approaching 0.4 W m<sup>-1</sup> K<sup>-1</sup> at 690 K. Interestingly, these values are similar to those measured in tetrahedrites although the physical mechanisms at play are distinct [8-19]. In tetrahedrites, Cu atoms occupy two different sites, one of which being in a slightly distorted trigonal planar coordination. The atomic thermal displacements of these Cu atoms are highly anisotropic and anharmonic due to the presence of active lone pair electrons on the neighbouring Sb atoms [11,30-33]. These displacements are associated with optical phonons that soften anomalously upon cooling thereby inhibiting thermal transport [30,33]. Such key crystallographic property that explains the glass-like  $\kappa_L(T)$  in tetrahedrites is lacking in colusites, which show a conventional crystalline behavior at low temperatures [23]. The very low  $\kappa_L$  values reached at high temperatures in colusites may be thus attributed to a more complex unit cell [20]. Further

inelastic neutron scattering experiments on colusites would be worthwhile to provide insights into the lattice dynamics of these compounds.

The resulting temperature dependences of the  $ZT$  values are shown in Figure 6. Maximum  $ZT$  values of 0.4 and 0.5 are achieved at 690 K in the Co and Ni sample, respectively. Hence, because of the marked metallic character of the Ni sample and the too high  $\rho$  values measured in the Co sample, the two compositions probed herein do not enable enhancing the  $ZT$  values with respect to the parent compound  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  [22].

## CONCLUSION

We report on the successful synthesis of polycrystalline colusites  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  with partial substitution of Ni and Co for Cu. The results evidence that Ni substitution leads to a more pronounced metallic character of the transport relative to Co, a fact likely explained by the higher Co concentration achieved. In agreement with prior studies, the lattice thermal conductivity is very low, reaching  $0.4 \text{ W m}^{-1} \text{ K}^{-1}$  at 690 K. However, the two compositions studied herein do not give rise to enhanced  $ZT$  values with a peak  $ZT$  value of 0.5 achieved at 690 K in  $\text{Cu}_{24}\text{Ni}_2\text{V}_2\text{Ge}_6\text{S}_{32}$ . Further optimization of the thermoelectric properties of these compounds might be realized by either varying the Co and Ni concentrations or by considering substitutions on the V, Ge or S sites of the crystal structure.



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## FIGURE CAPTIONS

Fig. 1. Perspective view of the cubic crystal structure of colusite  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$ . The Cu atoms are in blue, the V atoms are in red, the S atoms are in brown and the Ge atoms are in green. Some of the bonds between atoms are shown by grey cylinders.  $\text{CuS}_4$  (in blue) and  $\text{VS}_4$  (in red) tetrahedra are also shown. The Cu atoms are distributed over three distinct sites ( $6d$ ,  $8e$  and  $12f$ ) while vanadium,  $M$  and sulfur atoms are located on one ( $2a$ ), one ( $6c$ ) and two sites ( $8e$  and  $24i$ ), respectively. No distinction has been made for the Cu and S atoms distributed over the above-mentioned sites.

Fig. 2. Rietveld refinements of the PXRD pattern of the (a) Co and (b) Ni samples. In addition to the colusite phase, the secondary phases  $\text{Cu}_8\text{GeS}_6$  and  $\text{NiS}_2$  were included in the refinements for the Co and Ni samples, respectively. The vertical ticks mark the calculated reflections of the colusite (first row) and the secondary phase (second row). The baseline corresponds to the difference between the observed and calculated patterns.

Fig. 3. SEM images of the Ni (a) and Co (b) samples in the BSE mode along with the corresponding elemental X-ray maps.

Fig. 4. Electrical resistivity (a) and thermopower (b) versus temperature of  $\text{Cu}_{24}T_2\text{V}_2\text{Ge}_6\text{S}_{32}$  for  $T = \text{Ni}$  and  $\text{Co}$ .

Fig. 5. Temperature dependence of the total (a) and lattice (b) thermal conductivities of  $\text{Cu}_{24}T_2\text{V}_2\text{Ge}_6\text{S}_{32}$  for  $T = \text{Ni}$  and  $\text{Co}$ .

Fig. 6. Temperature dependence of the  $ZT$  values of  $\text{Cu}_{24}T_2\text{V}_2\text{Ge}_6\text{S}_{32}$  for  $T = \text{Ni}$  and  $\text{Co}$ .