Existence of pronounced ductility in $Rh_3A_xB_{1-x}$ and in $Rh_3B_xA_{1-x}$ materials

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***Abstract*—** In the present work, the comparative study is made between $Rh_3A_xB_{1-x}$ and in $Rh_3B_xA_{1-x}$ (A=V,Nb,Ta; B=Ti) (where x= 0, 0.125, 0.25, 0.75, 0.875, 1) materials. Here, the Rh_3V, Rh_3Nb and Rh_3Ta are taken as parent compounds and the ternary alloy addition is made by titanium with vanadium, niobium and tantalum. Electronic, elastic and mechanical properties are calculated for these compounds and the ductile/brittle analysis are made by using G/B ratio, Cauchy pressure and Poisson's ratio. Result shows that the following alloy combinations such that $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ are more ductile than their other respective combinations. All the calculated properties of $Rh_3Ti_x(V/Nb/Ta)_{1-x}$ compounds are compared with $Rh_3(V/Nb/Ta)_xTi_{1-x}$. By the way of detailed comparison we have entrenched that the existence of pronounced ductility in $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ combinations. This study is extended with calculating thermal properties such as Debye temperature, melting temperature and Grüneisen parameter and anisotropy factor, cohesive energy.

Keywords: Ab-initio study, Electronic band structure, intermetallics, mechanical property, ductility.

1. Introduction

Refractory metals and their alloys are used in various technological applications such as power generating devices, nuclear power reactors and space vehicles due to their superior high temperature properties. The refractory metals such as Nb, Ta, Mo, W and Re and some of the reactive metals such as Ti, Zr, Hf and V are already in use in nuclear power reactors. The difference between refractory metals and platinum group metals is subtle, and sometimes certain platinum group metals are classified as refractory group metals. Out of six Platinum Group Metals (PGMs), the most economically significant PGMs are platinum, palladium and rhodium. In these elements, rhodium has a higher melting point and lower density [1-3] than platinum. Rhodium alloyed with other PGMs used for furnace windings, bushing for glass fibre production, laboratory crucibles, electrodes for aircraft spark plugs and thermocouple elements. Similarly, titanium and its alloys are commonly used in the design of aircraft structures due to its excellent material properties.

Yamabe-Mitarai et al. proposed "refractory superalloys", based on high melting point fcc metals such as rhodium and iridium with $L1_2$ crystal structure [9] similar to Ni-based superalloys. The main research on such alloys has focused on the improvement of their ample properties and the extension of their practical applications. And also application of some intermetallic compounds for high temperature materials has been hampered due to their poor ductility. Hence it becomes necessary, a variety of alloys and composites are being studied as the replacement of traditional nickel-based superalloys for the jet engine and stationary gas turbines. Alloying has been considered as one of the most effective ways for designing of new materials.

In our previous work[10], we have started with the parent material Rh_3Ti and the ternary addition is made by V, Nb and Ta elements and it resulted in twelve combinations such as $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3V_{0.125}Ti_{0.875}$; $Rh_3Nb_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.125}Ti_{0.875}$ and $Rh_3Ta_{0.125}Ti_{0.875}$, $Rh_3Ta_{0.125}Ti_{0.875}$, $Rh_3Ta_{0.125}Ti_{0.875}$, $Rh_3Ta_{0.125}Ti_{0.875}$. From this study, we have identified the following three alloy combinations such as $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.75}Ti_{0.25}$ and $Rh_3Ta_{0.875}Ti_{0.125}$ are more ductile. We have aimed to entrench the above results theoretically.

Therefore, in this present study Rh_3V, Rh_3Nb and Rh_3Ta are taken as parent materials whereas Ti is doping element. Here, we have derived twelve ternary combinations namely $Rh_3Ti_{0.125}V_{0.875}$, $Rh_3Ti_{0.25}V_{0.75}$, $Rh_3Ti_{0.75}V_{0.25}$ & $Rh_3Ti_{0.875}V_{0.125}$ (V replaced by Ti); $Rh_3Ti_{0.125}Nb_{0.875}$, $Rh_3Ti_{0.25}Nb_{0.75}$, $Rh_3Ti_{0.75}Nb_{0.25}$ & $Rh_3Ti_{0.875}Nb_{0.125}$ (Nb replaced by Ti) and $Rh_3Ti_{0.125}Ta_{0.875}$, $Rh_3Ti_{0.25}Ta_{0.75}$, $Rh_3Ti_{0.75}Ta_{0.25}$ & $Rh_3Ti_{0.875}Ta_{0.125}$ (Ta replaced by Ti). A first-principles calculation based on the density-functional theory was conducted to investigate the structural, electronic and mechanical properties of these twelve newly proposed compounds. The ductility of these compounds was analyzed and compared with our previous study for $Rh_3A_xB_{1-x}$ (A=V,Nb,Ta; B=Ti) [10]. The same three alloy combinations such as $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ are are identified as more ductile in either way.

2. Method of calculations

All the calculations have been carried out by using the full potential linearized augmented plane wave (FP-LAPW) method using wien2k code[11]. The exchange correlation potential is calculated by the generalized gradient approximation (GGA) in the scheme of Perdew, Burke and Ernzrhof (PBE) [12]. The k-point mesh of the Brillouin zone is performed using Monkhorst-Pack [13] scheme with 11 x 11 x 11 for parent compounds and 10 x 10 x 10 for supercells. The convergence criteria are as follows which are same with our previous work [10]: the energy change is converged below 0.0001eV, charge is converged below 0.001Ry, R_{MT} x K_{max} = 7, l_{max} = 10 and G_{max} = 12.

2. Results and discussion

2.1. Summary of previous study

In our previous study [10], structural, electronic, elastic and mechanical properties of $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3V_{0.25}Ti_{0.75}$, $Rh_3V_{0.75}Ti_{0.25}$, $Rh_3V_{0.875}Ti_{0.125}$; $Rh_3Nb_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.25}Ti_{0.75}$, $Rh_3Nb_{0.75}Ti_{0.25}$, $Rh_3Nb_{0.875}Ti_{0.125}$ and $Rh_3Ta_{0.125}Ti_{0.875}$, $Rh_3Ta_{0.25}Ti_{0.75}$, $Rh_3Ta_{0.75}Ti_{0.25}$ and $Rh_3Ta_{0.875}Ti_{0.125}$ combinations are calculated. Using elastic constants, the various parameters

such as bulk modulus (B), shear modulus (G), Young's modulus (E), Cauchy pressure (C_{12}-C_{44}), G/B ratio, Poisson's ratio (ν) and hardness (H_v) values were calculated (Refer Table 1 in Ref.[10]). From this study, we have identified the following three alloy combinations $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.75}Ti_{0.25}$ and $Rh_3Ta_{0.875}Ti_{0.125}$ are more ductile having highest Cauchy pressure and ν value and lowest shear modulus, Young's modulus and G/B values.

2.2. Present study

2.3.

The rhodium-based intermetallic compounds Rh_3V, Rh_3Nb and Rh_3Ta have a Cu_3Au-type structure (space group: Pm3m, No: 221). The constituent atom V/N/Ta is located at the site (0,0,0) and the Rh atom is located at the site (0,0.5,0.5). Using GGA method, the calculated lattice parameters and bulk modulus values for $Rh_3Ti_xV_{1-x}$, $Rh_3Ti_xNb_{1-x}$ and $Rh_3Ti_xTa_{1-x}$ (where x= 0, 0.125, 0.25, 0.75, 0.875, 1) are listed in Table 1. It can be clearly seen that the calculated results are in good agreement with the available theoretical and experimental data. The percentage of error between the calculated and the experimental lattice constant is 0.3, 1.07 and 0.9 for Rh_3V, Rh_3Nb and Rh_3Ta respectively.

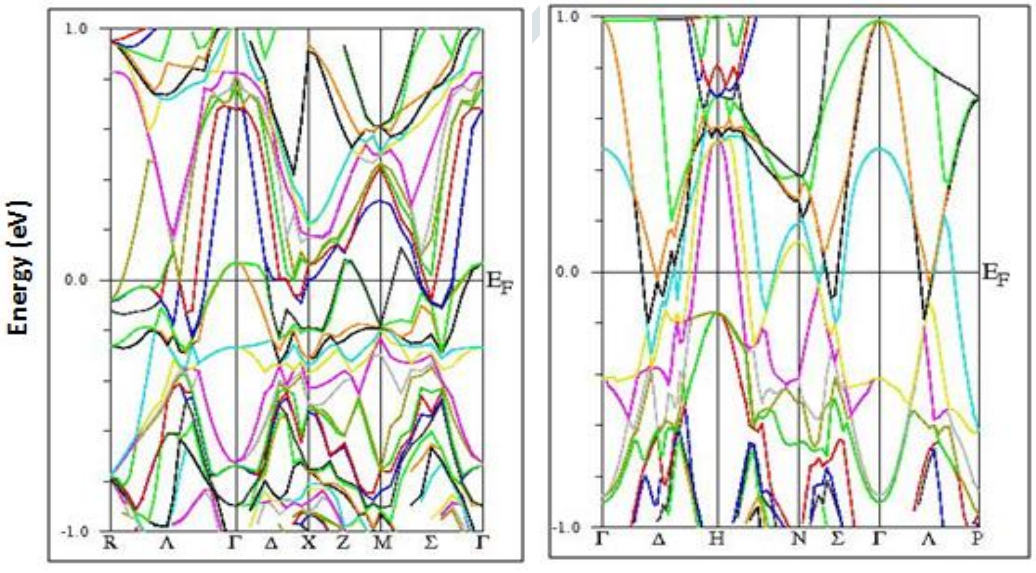
Our calculated results for elastic constants in Table 2 satisfy the mechanical stability conditions for cubic crystals namely, $C_{11}>0$, $C_{12}>0$, $C_{11}-C_{12}>0$, $C_{11}+2C_{12}>0$ and $C_{12}>B<C_{11}$. As in our previous study [10], the same parameters (elastic constants (C_{11}, C_{12} and C_{44}), Young's modulus (E), bulk modulus (B), Shear modulus (G), Cauchy pressure (C_{12}-C_{44}), Pugh criterion (G/B), Poisson's ratio (ν) and hardness (H_v)) are calculated for all these compounds and presented in Table 1. Additionally calculated anisotropy factor (A), Debye temperature (θ_D), melting temperature (T_m) and Grüneisen parameter (ζ) values are presented in Table 2.

Ductility of these compounds can be predicted by using Cauchy pressure [15], G/B ratio [16] and ν [17] values. According to the ductile/brittle analysis [10], the following three combinations $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ are identified as more ductile materials having highest positive Cauchy pressure 102.45 GPa, -6.79 GPa and 34.78 GPa, less than 0.57 G/B ratio 0.33, 0.56 and 0.51and greater than 0.25 ν values such that 0.35, 0.25 and 0.28respectively.

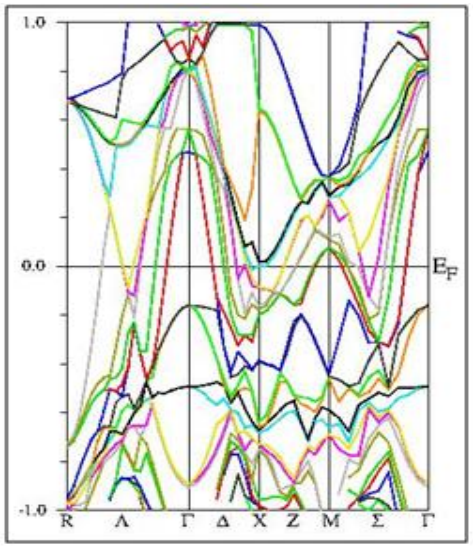
Bulk modulus of $Rh_3Ti_xV_{1-x}$, $Rh_3Ti_xNb_{1-x}$ and $Rh_3Ti_xTa_{1-x}$ (where x= 0, 0.125, 0.25, 0.75, 0.875, 1) combinations are linearly decreases. Since bulk modulus is associated with cohesive energy (or) binding energy of atoms in crystal, it could be used as a measure of average bond strength [18]. Thus the addition of Ti to Rh_3V, Rh_3Nb and Rh_3Ta can significantly decrease the atomic bond strength [19]. The shear modulus and Young's modulus values of these alloys also decreases when Ti is acting as doping element. Therefore, the lowest values of G and E in $Rh_3Ti_{0.875}V_{0.125}$ (80.47 GPa & 216.83 GPa), $Rh_3Ti_{0.25}Nb_{0.75}$ (160.78 GPa & 400.69 GPa) and $Rh_3Ti_{0.125}Ta_{0.875}$ (134.87 GPa & 345.51 GPa) combinations indicating that the increase of ductility (decrease of brittleness).

Hardness is related to the plastic and elastic properties of materials. From Table 2, it shows that the $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ materials having low hardness value than other respective combinations. The elastic anisotropy is another important physical property of material, is an indicator of the degree of anisotropy in the solid structures. The anisotropy factor A= $(2C_{44}+C_{12})/C_{11}$, A=1 implies an isotropic material, when the value of A is larger (or) smaller than unity indicates the measure of the degree of elastic anisotropy [20]. From these calculated parameters, the three following materials namely $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ are identified as more ductile materials than their respective series of combinations. The same three materials were identified as more ductile materials from our previous study [10] whereas Rh_3Ti as parent and V/Nb/Ta elements were considered as doping elements. Hence, theoretically we have enriched our result by both ways which may be experimentally possible.

In this part, we have presented the band structure and DOS histograms of the more ductile combinations that are shown in Fig. 1(a-c) and 2(a-c). From Fig. 1a (for $Rh_3Ti_{0.875}V_{0.125}$ & $Rh_3Ti_{0.125}Ta_{0.875}$), one can observe that few d states of V and Ti interact with each other between the k-points 'R' and 'Λ' at close vicinity of the Fermi level, whereas in Fig. 1b, the Ta and Ti atom interaction shifted down from the Fermi level. As in case of $Rh_3Ti_{0.25}Nb_{0.75}$ (Fig.1c), the 'd' states of Ti and Nb interact with each other between k-points 'Λ' and 'P' slightly shifted downwards.



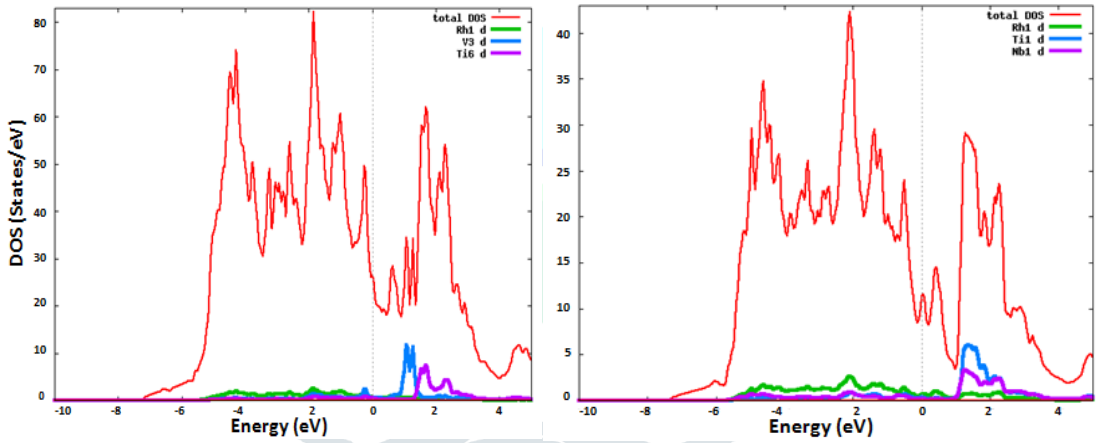
(a) (b)



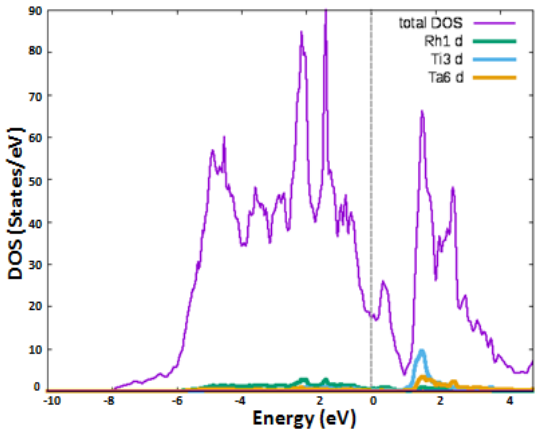
(c)

Fig. 1 Band Structure of (a) $Rh_3Ti_{0.875}V_{0.125}$ (b) $Rh_3Ti_{0.25}Nb_{0.75}$ & (c) $Rh_3Ti_{0.125}Ta_{0.875}$

From Fig. 2(a-c), it can be clearly seen that the three alloy combinations exhibit metallic characteristics because there is no energy gap near the Fermi level. The calculated TDOS is mainly dominated by Rh-d, Ti-d and V/Nb/Ta-d state, while Rh- s, p, Ti- s – p and V/Nb/Ta –s-p states have few contribution. From Fig. 2(a-c), it is observed that the peaks in the TDOS that lie below the Fermi level are mainly due to Rh- d states and above the Fermi level are mainly due to corresponding 'd' states of Ti and V/Nb/Ta atoms. There is a strong hybridization between Ti- d and V-d states (Fig. 2a), Ti-d and Nb- d states (Fig. 2b) and Ti- d and Ta- d states (Fig.2c) near the Fermi level.



(a) (b)

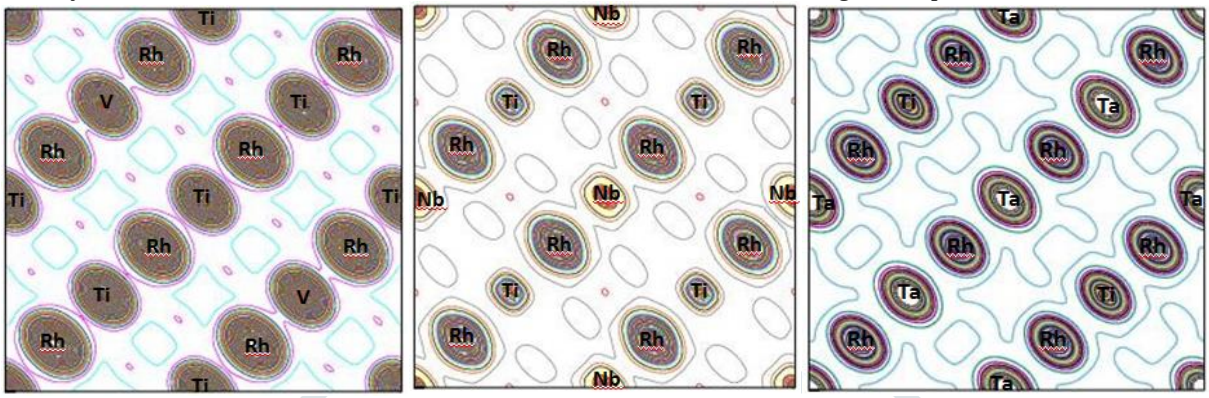


(c)

Fig. 2 Total and partial density of states (a) $Rh_3Ti_{0.875}V_{0.125}$ (b) $Rh_3Ti_{0.25}Nb_{0.75}$ & (c) $Rh_3Ti_{0.125}Ta_{0.875}$.

From electronic properties study, we have revealed that the very similar band structure and DOS histograms of $Rh_3V_{0.125}Ti_{0.875}$, $Rh_3Nb_{0.75}Ti_{0.25}$ and $Rh_3Ta_{0.875}Ti_{0.125}$ alloys in either ways.

Study on bonding nature of alloys could be useful in investigation the ductile/brittle nature. The ductile materials show metallic bonding character whereas the brittle materials show covalent bonding nature (strong directional characteristics of bonding). The charge density plots of $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$ combinations are shown in Fig.3(a-c). From Fig.4a, Fig.4b and Fig.4c, it can be noted that the electron contour enclosing Rh and V/Nb/Ta reveals that the presence of directional character of bonding present in Rh_3V, Rh_3Nb and Rh_3Ta. There is a considerable decrease in directional bonding when V/Nb/Ta atoms are replaced by Ti atoms. In Fig. 3(a), electron density contours enclosing Rh and V are diminished when Ti atom occupies the place of V atom. This makes the directional bonding very weak; it may attribute to the ductile nature of the material. In the same way, the addition of Ti to Rh_3Nb and Rh_3Ta reduces the directional bonding nature present in Rh_3Nb and Rh_3Ta.



(a) (b) (c)

Fig. 3 Charge density plot of (a) $Rh_3Ti_{0.875}V_{0.125}$ (b) $Rh_3Ti_{0.25}Nb_{0.75}$ & (c) $Rh_3Ti_{0.125}Ta_{0.875}$.

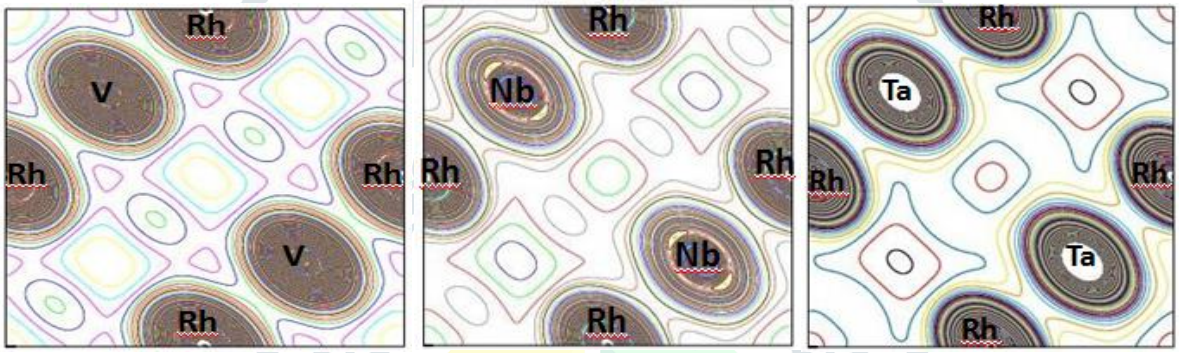


Fig. 4 Charge density plot of (a) Rh_3V (b) Rh_3Nb & (c) Rh_3Ta.

Conclusion

Ab initio calculations of structural, electronic and elastic properties for $Rh_3Ti_x(V,NbTa)_{1-x}$(x= 0.125, 0.25, 0.75, 0.875) materials have been studied. The present calculations theoretically entrenched our results that the same alloy combinations $Rh_3Ti_{0.875}V_{0.125}$, $Rh_3Ti_{0.25}Nb_{0.75}$ and $Rh_3Ti_{0.125}Ta_{0.875}$are found to be more ductile in both ways having higher values of Cauchy pressure, and Poisson's ratio and lower values of shear modulus and Young's modulus considerable hardness. And also a brittle to ductile transition is observed in Rh_3V, Rh_3Nb & Rh_3Ta, when Ti is added. Electron density plots of these compounds revealed that the existence of pronounced ductility in these compounds.

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