

In situ variable temperature X-ray diffraction studies on size scale of CuCrO_2 polytypes with delafossite structure

D. URSU^{a,b}, M. MICLEĂU^b, I. GROZESCU^{a,b}

^aPolitehnica University of Timisoara, Romania

^bNational Institute for Research and Development in Electrochemistry and Condensed Matter Timisoara, Romania

We had first studied the thermal stability of 2H and 3R polytypes of CuCrO_2 nanocrystals obtained by hydrothermal method from room temperature up to 1100 °C under vacuum conditions. The variable temperature X-ray patterns had shown that the thermal stability depends by the polytypes of CuCrO_2 nanocrystal, 2H- CuCrO_2 has been more stable phase than 3R- CuCrO_2 . Also, our work had revealed the effect of the synthesis method on the thermal stability of 3R- CuCrO_2 microcrystals obtained by hydrothermal method and conventionally solid state method. An interesting result is that synthesis method has no effect on the thermal stability of 3R- CuCrO_2 delafossite phase, the decomposition temperature has been found about 1000°C. High temperature X-ray patterns of 3R-nano and micro crystals had shown the size dependence thermal stability, the 3R- CuCrO_2 micro crystal had kept the delafossite structure up to 1000°C compared with 500°C for 3R- CuCrO_2 nanocrystal.

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1. Introduction

The search for new thermoelectric materials in order to convert waste heat into electricity has motivated numerous studies on transition-metal oxides. One advantage of these materials over other classes of materials lies in their stability at elevated temperatures in air [1]. Today thermoelectric materials [2-4] have shown they are very good sources of energy and therefore over time to be shown that such materials Bi_2Te and PbTe have a high value of figure of merit however they also have some disadvantages such as the decomposition in air and high temperature oxidation [5]. In fact heavy metals like BiTe and TePb are expensive and toxic [6]. This can lead to limited use in practical applications of thermoelectric materials to generate electricity. CuCrO_2 is the most promising Cu-based delafossite for p-type optoelectronic devices [7], batteries [8] and p-type conducting oxides [9]. Various methods have been employed for the synthesis of CuCrO_2 such as solid state reaction [10], flux deposition [11], hydrothermal method [12,13], pulsed laser deposition [14], rf sputtering [15], chemical vapor deposition [16], monomode microwave heating method [17]. The delafossite structure can be visualized as consisting of two alternate layers: a planar layer of A cation in a triangular pattern and a layer of edge-sharing BO_6 octahedra flattened with respect to the *c*-axis. Depending on the orientation of each layer in stacking, two crystalline forms can exist. By stacking the double layers with alternate A layers oriented 180° relative to each other, the hexagonal 2H type is formed which has $P63/mmc$ space group symmetry. If the double layers are stacked with the A layers oriented in the same direction relative to one another

but offset from each other in a three layer sequence, the rhombohedral 3R type is formed that has the space group symmetry of $R\bar{3}m$. [18]. Currently, in situ VT-XRD has been extensively employed to study the formation or characterization of PbTiO_3 [19], BaTiO_3 [19], calcium phosphate [20], hydroxyapatite (HA) [21,22], sodium yttrium fluoride [23], Bi_2MoO_6 [24], CoAl_2O_4 [24], silicon nitride compounds [25], and others. This technique offers an opportunity to follow thermodynamic phase changes at elevated temperatures.

2. Experimental

2.1. Material preparation

All chemical reagents in this experiment were of analytical grade and used without further purification. For hydrothermal synthesis we used cuprous oxide (Cu_2O) and hydrated chromium trioxide (CrO_3) which is purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) is purchased from Silal Trading and was used for control pH and the product solubility [26]. $\text{Cr}(\text{OH})_3$ amorphous was obtained from $\text{Cr}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ and NaOH. For solid state synthesis the cuprous oxide (Cu_2O) and Cr_2O_3 which is purchased from Sigma-Aldrich. In the synthetic procedure of the hydrothermal method for obtaining phase pure CuCrO_2 nanocrystals 2H and 3R we used 1mm Cu_2O and 2mm $\text{Cr}(\text{OH})_3$ and the molarity of NaOH range between 0.3 and 3.5M, temperature range from 200°C to 250 °C, reaction time 48 and 60 hours in an aqueous solution. At low temperature 200°C, reaction time 60h and 1M NaOH was obtained 2H- CuCrO_2 pure

phase. If we increasing the temperature and the molarity of NaOH was found 3R- CuCrO₂ pure phase. For synthesis a pure phase 3R-CuCrO₂ microcrystals was used 1mmol Cu₂O, 2 mmol CrO₃ hydrat phase and 2.5M NaOH. In this time temperature synthesis is 300 °C, reaction time is 48h. Pure phase 3R-CuCrO₂ from solid state synthesis was obtaining at temperature of 1100 °C from Cu₂O and Cr₂O₃. In case of samples prepared from hydrothermal method at high temperature (> 250 °C) and pressure (> 100 bars), the as prepared solution was tight sealed in SS autoclave (12NiCr250) and placed in high temperature furnace. For the low temperature synthesis (≤ 250°C), samples were prepared in teflon autoclaves. After the given reaction time, all the autoclaves was taken out and allowed to cool at room temperature. The precipitate was filtered and washed with absolute alcohol and deionized water in sequence for several times. The product was dried in an oven at 80 °C for 5h.

2.2. Characterization

The resultant powder was characterized by powder X-ray diffraction (XRD) data were collected with a PANalytical X'pert Pro diffractometer using the CuK α radiation ($\lambda = 0.1542$ nm). The diffraction patterns were recorded in the [10°–80°] (2θ) angular range, using 0.013 (2θ) step and a constant counting time of 165 s/step. A Scanning Electron Microscope (SEM) was used to observe the microstructure of the as synthesized powder sample. The effect of heat treatment on the structure of the materials, prepared in different mode (solid state and hydrothermal), the compound CuCrO₂ was followed in-situ by XRD, thanks to a variable temperature chamber (Anton Paar HTK 2000 high temperature chamber), connected to the diffractometer. These experiments allow to obtain more insight on the composition of the materials. The sample was heated at the rate of 10 °C/min, and diffraction spectrum of a sample was one hour were performed every 100 °C, from RT to 1100 °C. Inside the chamber is a vacuum with value 10⁻⁴ mbar. This vacuum is made with vacuum pump (TRIVAC B D4B/D83) to the value of 10⁻² and with turbo pump (TURBOVAC 50) to value 10⁻⁴.

3. Results and discussion

Fig. 1 shows the XRD result of the 3R CuCrO₂ nanocrystals target prepared by the hydrothermal method. It can be observed that the target is a single delafossite-structured 3R-CuCrO₂ nanocrystals phase without any undesired phases. The corresponding JCPDF Card No. of 3R CuCrO₂ is (00-039-0247). The crystalline size can be calculated using the Scherrer formula [27],

$$D = \frac{k\lambda}{B \cos \theta}$$

where k is a constant (~ 1), B is the full width at half maximum (FWHM), λ is the wavelength of X-ray and θ is

the diffraction angle. The crystalline size of the target is about 20 nm.

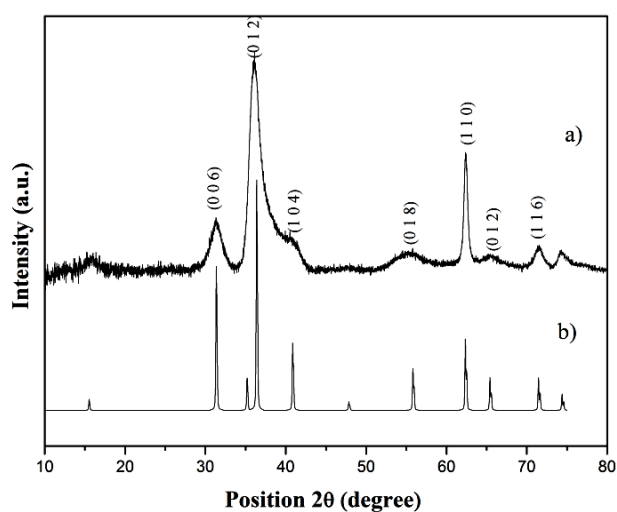


Fig. 1. X-ray diffraction pattern: a) 3R-CuCrO₂ laminar nanocrystals b) The standard data for 3R-CuCrO₂ reference cod 00-039-0247

Fig. 2 shows the XRD result of the 2H-CuCrO₂ nanocrystals target prepared by the hydrothermal method [28]. The relative stronger diffraction peaks at ($2\theta = 31.39^\circ, 35.68^\circ$ and 62.26°) are corresponding to (0 0 4), (1 0 0) and (1 0 5) planes of 2H-CuCrO₂, respectively. No peaks corresponding to CuO, Cu₂O, Cr(OH)₃ families can be detected. The crystalline size was calculated also with Scherrer formula. The crystalline size of the target is about 20 nm. Fig. 3 shows the XRD result of the 3R-CuCrO₂ microcrystals target prepared by the hydrothermal method. From the diffraction spectrum can be seen that the sample crystallinity increased when the temperature increases.

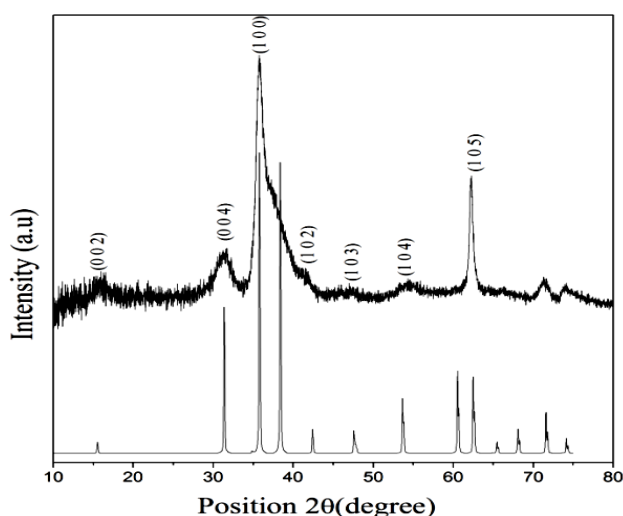


Fig. 2. X-ray diffraction pattern: a) 2H-CuCrO₂ laminar nanocrystals b) The standard data for 2H-CuCrO₂ reference cod 01-089-0540

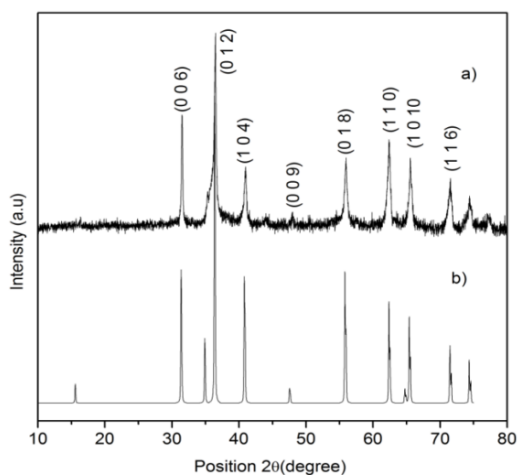


Fig. 3. X-ray diffraction pattern: a) 3R-CuCrO₂ microcrystals b) The standard data for 3R-CuCrO₂ reference cod 00-026-1113

It can be observed that the target is a single delafossite structured 3R-CuCrO₂ microcrystals phase without any undesired phases. The corresponding JCPDF Card No. of 3R-CuCrO₂ is (00-026-1113). Using solid state method to obtain phase-pure 3R-CuCrO₂ (figure 4) which is according with [10]. From XRD spectrum can be seen that there is no impurities and the intensity of peak is very high, this intensity is due to high temperature to obtain.

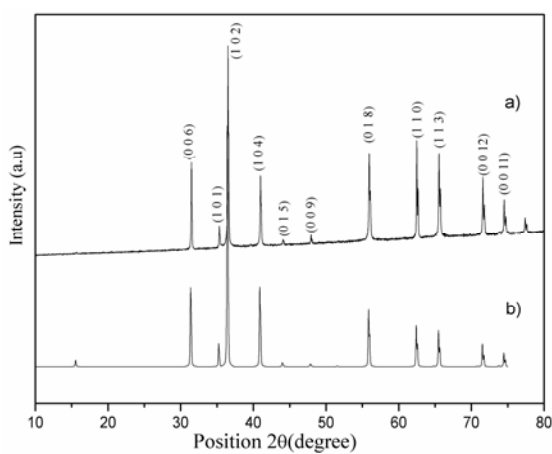


Fig. 4. X-ray diffraction pattern: a) 3R-CuCrO₂ microcrystals b) The standard data for 3R-CuCrO₂ reference cod 00-089-0539

Fig. 5 shows the morphology of CuCrO₂ compounds nano and micro size from hydrothermal synthesis for all the sample. In picture 5a and 5b we can see that particles are nanometer size. With increasing temperature (around 300°C) started to rise and particle size is 1-2μm, (fig.5c) and continue to grow (fig.5d). In figure 6 shows in situ HT-XRD has been performed on the compounds 3R-CuCrO₂ nanocrystals obtained from hydrothermal method at low temperature. The sample was placed inside a high temperature chamber, connected to the diffractometer. For study the thermal stability sample was heated at different temperatures from room temperature up to temperatures of 1100 °C.

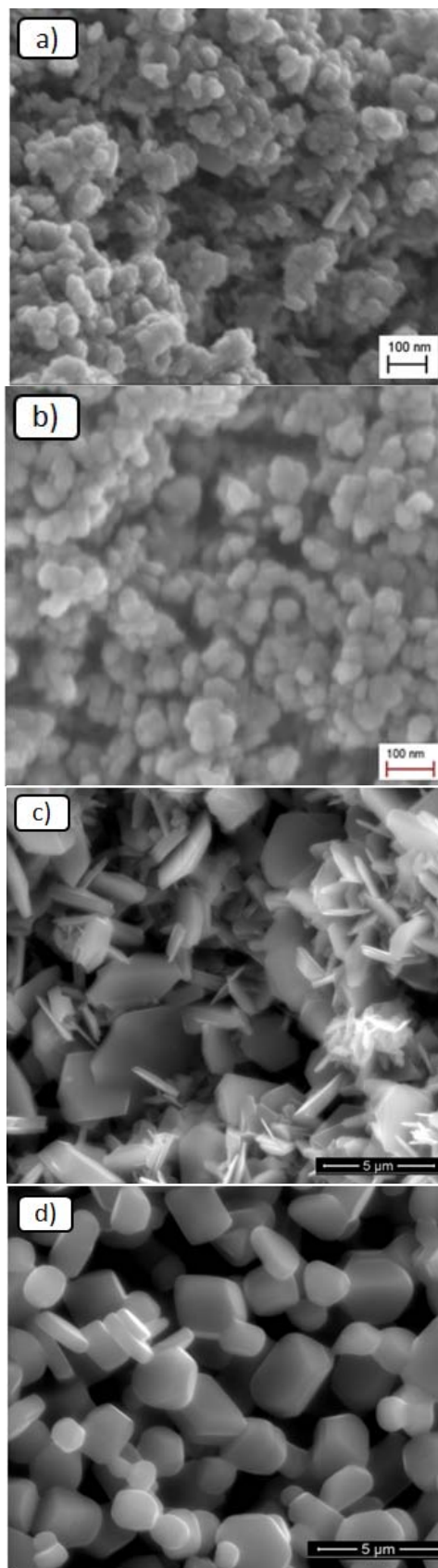


Fig 5. SEM images of the compound CuCrO₂: a) 3R-CuCrO₂ nanocrystals, b) 2H-CuCrO₂ nanocrystals, c) 3R-CuCrO₂ microcrystals and d) 3R-CuCrO₂ microcrystals

As can be seen from (Figure 5) 3R- CuCrO_2 nanocrystals compound is stable up to temperatures of 500 °C, where the value ($2\theta = 43.384^\circ$) is a little Cu metal peak with reference code (00-004-0836), which increases in intensity with increasing temperature. At temperature of 600 °C there is another little Cu metal peak the value ($2\theta = 50.528^\circ$) also belonging to the same reference code (00-004-0836), its intensity being maintained until 1100 °C. Between temperature 700 °C and 1100 °C appears phase Cu_2O_3 belonging reference code is (00-001-1294) whose peaks at ($2\theta = 24.732^\circ, 34.139^\circ, 41.933^\circ, 55.329^\circ, 63.640^\circ, 67.373^\circ, 73.592^\circ$). The rest unidentified peaks are the compound CuCrO_2 . Platinum peak at ($2\theta = 40.766^\circ, 47.327^\circ, 69.005^\circ$) is given the support that it provides sample.

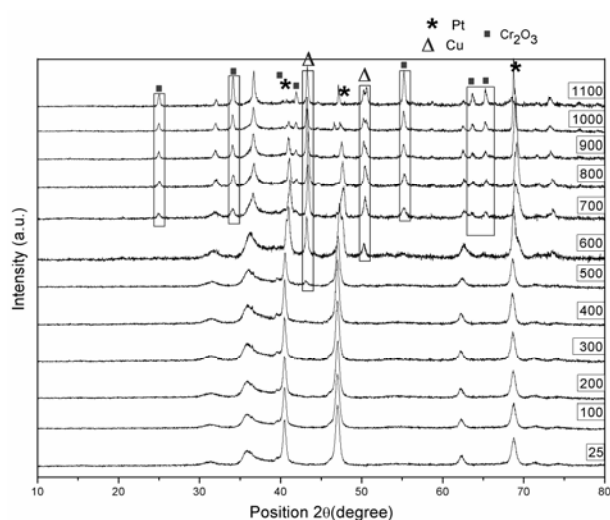


Fig. 6. X-ray diffraction patterns of phase evolution at different temperatures (3R- CuCrO_2 nanocrystals)

Fig. 7 shows diffraction patterns of phase evolution at different temperatures 2H- CuCrO_2 nanocrystals. As you can see the first little belonging Cu metallic impurity with reference code is (00-004-0836) temperature of 600 °C, which remarkable is that 2H- CuCrO_2 phase stability is better than 3R CuCrO_2 phase stability. Temperatures between 700 °C and 1100 °C appears Cu_2O_3 phase whose peaks appear as well as the 3R-phase CuCrO_2 . However, with forming a vacuum at higher than 500°C, some Cu ion was reduced to Cu metal phase, in both cases CuCrO_2 2H and 3R, same thing happened with [29] when using a controlled gas environment (mixture of 5% hydrogen in nitrogen gas). For this reason was stopped formation of phase CuCr_2O_4 in case when heat treatment would be in the air, without a controlled environment at temperatures of 700°C appears CuCr_2O_4 phase, conform phase diagram reported by Jacob et al. [30] and an impurity of CuO , because at higher temperature and reduced oxygen partial pressure, Cu^{2+} reduces to Cu^+ [31].

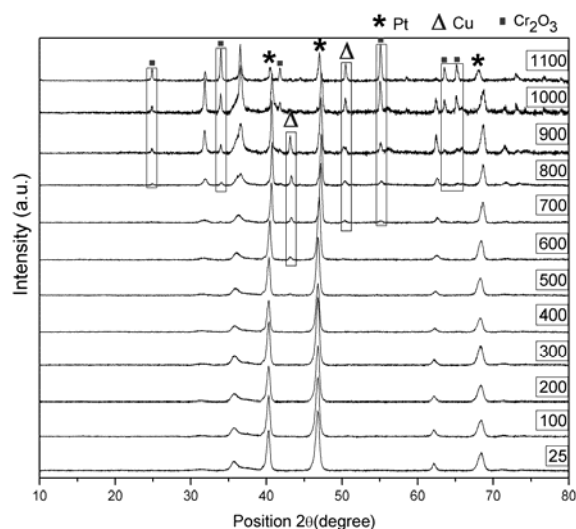


Fig.7. X-ray diffraction patterns of phase evolution at different temperatures (2H- CuCrO_2 nanocrystals)

Fig. 8 shows diffraction patterns of phase evolution at different temperatures 3R- CuCrO_2 microcrystals from hydrothermal method at high temperature (300°C). As you can see the pure phase is stable up to temperatures of 900°C. At a temperature of 1000°C there are two peaks of Cr_2O_3 at ($2\theta = 24.732, 34.139$), with code reference 00-001-1294. Comparing with 3R- CrCrO_2 nanocrystals phase can be seen as 3R- CrCrO_2 microcrystals phase is more stable. We think this stability depends mainly on the temperature at which the synthesis and particle size.

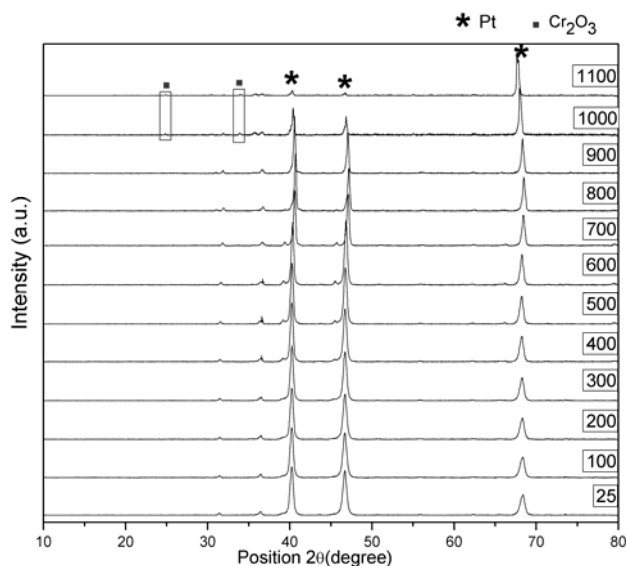


Fig.8. X-ray diffraction patterns of phase evolution at different temperatures (3R- CuCrO_2 microcrystals)

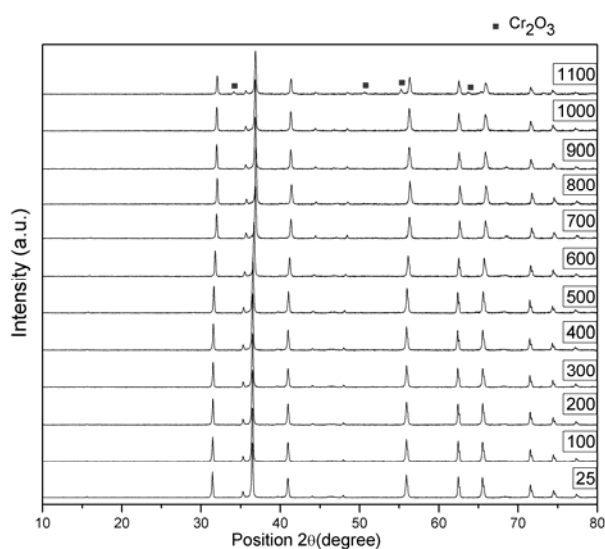


Fig. 9. X-ray diffraction patterns of phase evolution at different temperatures (3H-CuCrO₂ microcrystals) from solid state method

Fig. 9 shows diffraction patterns of phase evolution at different temperatures 3R-CuCrO₂ microcrystals from solid state method. As you can see the pure phase is stable up to temperatures of 1000°C. Only at the temperature of 1100 ° C is impurity of Cr₂O₃. CuCr₂O₄ intermediary phase does not occur, due to the controlled environment inside the TH-XRD camera.

4. Conclusions

CuCrO₂ compound was prepared by two methods such hydrothermal and solid state. The particles are nanosize and microsize which can be seen both in the diffraction spectra and the SEM images. Crystallization process of CuCrO₂ compound nano and microsize, and different polytypes was examined in detail by in-situ high-temperature X-ray diffraction method (HT-XRD) in the temperature range of 25–1100°C in vacuum. It was found that crystallization process was highly influenced by the effect of vacuum because inhibit the formation of CuCr₂O₄ phase, as an intermediate in the formation of phase pure CuCrO₂. Size particles is the main factor affecting the stability of pure phase, which is more stable for CuCrO₂ microsize than for CuCrO₂ nanosize compound. CuCrO₂ thermal stability of the compound obtained by solid state method is as stable as obtained by hydrothermal method, appearance impurities Cr₂O₃ are only temperatures 900-1000°C. In the future, will try doping CuCrO₂ with transition materials from hydrothermal method, where there are very few publications and check the thermal stability due to doping material.

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*Corresponding author: ioan.grozescu@icmct.ro