

RESEARCH PAPER

## Luminescence and scintillation characterization of Silver doped KCl single crystal grown by Czochralski technique for photonic applications

Sanaz Alamdari<sup>1</sup>, Mohammad Hemmati<sup>2</sup>, Majid Jafar Tafreshi<sup>2\*</sup>, Morteza Sasani Ghamsari<sup>3</sup>, Hosein Afarideh<sup>4,\*\*</sup>, Aghil Mohammadi<sup>4</sup>, Yoon Sang Kim<sup>5</sup>, Mohammad Hosein Majles Ara<sup>6</sup>

<sup>1</sup> Semnan University, Semnan, Iran

<sup>2</sup> Faculty of Physics, Semnan University, Semnan, Iran

<sup>3</sup> Photonics and Quantum Technologies Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

<sup>4</sup> Department of Energy Engineering and Physics, Amirkabir University of Technology, Tehran, Iran

<sup>5</sup> Department of Computer Science and Engineering, Korea University of Technology and Education, Cheonan, South Korea

<sup>6</sup> Applied Science Research Center(ASRC), Kharazmi University, Tehran, Iran

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### ABSTRACT

In this study, the scintillation and optical properties of pure and silver doped potassium chloride (KCl:Ag) single crystals were reported. Pure and doped KCl bulk single crystals with a good optical quality and free from cracks were grown from the melt using Czochralski technique. Different analysis methods were used to study the optical and scintillation properties of the grown crystals. The XRD, EDX and SEM results confirmed the formation of KCl compound. The UV excitation, X and gamma rays were employed to evaluate the scintillation and optical properties of the synthesized samples. The X-ray induced luminescence spectrum of doped crystal showed the prominent blue emission at 400-460 nm wavelength region. Also, the thermoluminescence response of doped sample showed a strong TL glow peak at 200 and proper linear ranges as a function of dose making it a promising candidate for dosimetry and photonic applications.

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### INTRODUCTION

After one century from the beginning of the crystal growth technique, many efforts have been devoted to use this procedure for growth of different single crystals with wide range of applications. Among all single crystals, scintillator crystals have gained a lot of attention, and many attempts have been made to grow their single crystals with highly potential for widespread applications including medical imaging, dosimetry, nuclear detectors and homeland security [1]. Up to now, several techniques have been developed

to grow single crystals, and Czochralski method (CZ) is one of the most common used techniques to grow such high-quality single crystals [2-6]. For example, potassium chloride (KCl) crystal is one of the promising transparent crystals which can be grown easily from the melt. KCl is one of the alkali halide crystals having wide band gap (~8 eV), simple cubic structure, transparent in the UV-Vis and near-IR regions [7]. Improvement of the luminescence properties of KCl single crystals doped with suitable impurity opens up new perspectives in their dosimetric applications [7-11]. The ionic radius of K<sup>+</sup> is 1.33Å, therefore

\* Corresponding Author Email: : [mtafreshi@semnan.ac.ir](mailto:mtafreshi@semnan.ac.ir),  
[hafarideh@unt.ac.ir](mailto:hafarideh@unt.ac.ir)

it has a great area of possible doping impurities with different sizes and different concentrations into the lattice [8]. Doping is the intentional introduction of impurities into a lattice for the point of modulating its properties; Indeed, dopants can enhance the electrical, optical and structural properties of the host material [9- 11]. The introducing of defects associated with especial dopant acting as a shallow level or trap states, can modify the luminescence characteristics of KCl crystals. For example, silver as an attractive dopant can change valence level of host crystal during irradiation. Silver has a large electron affinity that acts as cations in host material. So, a possible enhancement in thermoluminescence (TL), photoluminescence (PL) and X-ray induced luminescence (XRIL) emission is anticipated by doping KCl with suitable amount of silver ions [2]. Krishnakumar reported the growth and prospering of optical properties of Ag and rare earth co-doped KCl single crystals [2]. Kawai and Hirai showed that the silver centers have important role in luminescence properties of KCl single crystals [5]. Although there are lots of studies on the optical investigations of KCl crystals with different dopants, no study has been performed on the luminescence properties under all three UV, X-ray and thermo excitation. In this work, pure KCl and KCl: Ag crystals have been grown by Czochralski technique. Scintillation characteristics including photo-thermo and X-ray stimulated luminescence were performed on the pure and doped crystal. The results showed that cost-effective KCl: Ag crystal is very suitable for optical device applications and

dosimeters.

## EXPERIMENT

The growth of crystals was carried out using Czochralski method. A KCl single crystal with 2 cm length and 1 cm diameter was used as a seed. The seed was tied onto an alumina pulling rod using platinum wire through scratching the grooves on the seed. 50 gr KCl (Merck 99.5%) and 0.5 gr AgCl (Merck 99.5) powders were mixed and put in crucible and temperature raised to 830°C. When the equilibrium condition on the melt was satisfied, the seed was brought in contact to melt and the necking was performed at the pulling rate of 10 mm/h and rotation rate of 31 rpm. In order to form the shoulder of the crystal, the temperature was decreased to 830°C at the rate of 10 °C/h. Finally, the crystal was pulled up at the speed of 85 mm/h to separate it from the melt and calcined at 550°C for 8 h. The crystals were cut into some pieces for required characterization; brief of the process is shown in Fig. 1. The X-ray diffraction (XRD) analysis for structural investigation was carried out by D8-Advance Bruker Cu K ( $\lambda=0.15406$  nm). Field emission scanning electron microscopy FESEM (model MIRA3TESCAN-XMU) with energy dispersive X-ray analysis (EDX) was performed to investigate the morphology, particle size and chemical composition of sample. Optical properties of the crystals were studied by the UV-visible spectrophotometer (Perkin Elmer) and photoluminescence (Varian Cary Eclipse fluorescence) with exciting wavelength of 230 nm. The X-ray luminescence study was performed

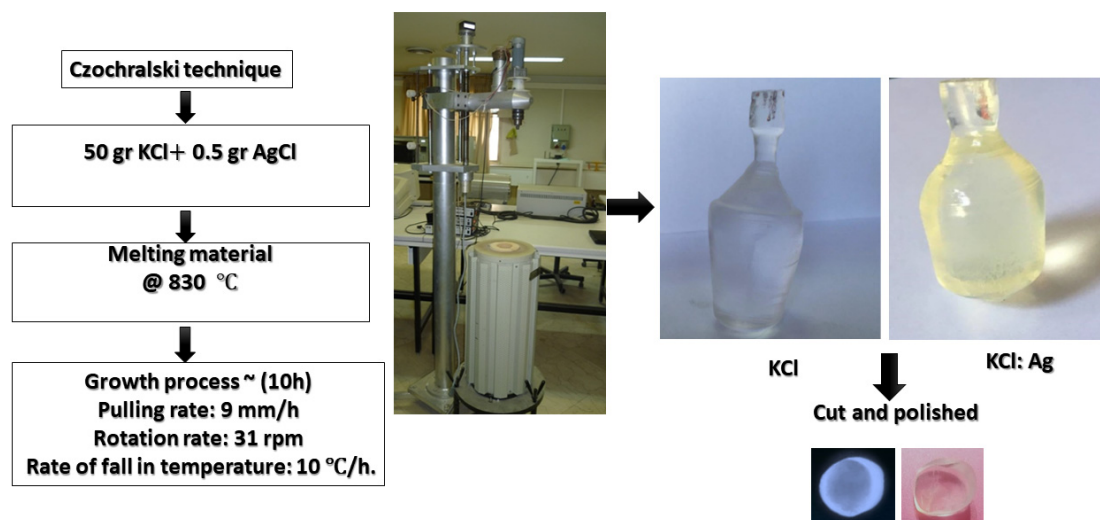


Fig. 1: Brief schematic of the fabrication process.

using a Cu X-ray tube at 35 kV<sub>p</sub> for a 30s. The samples were also exposed to <sup>60</sup>Co source and their thermoluminescence (TL) properties were investigated.

**RESULTS AND DISCUSSION**

**XRD**

The crystalline nature and structure of the grown crystals were characterized by X-ray diffraction technique. The X-ray diffraction pattern of pure and doped crystals are shown in Fig. 2 showing a very good agreement with XRD reference code JCPDS-01-075-0296. All *hkl* planes

in the spectra were indexed. The results revealed a crystalline nature for the samples. The orientation of the highest intensity peak is found to be along (200) plane located at 2θ =28.34 of KCl [11]. It was observed that the intensities of the XRD peaks increased slightly by introducing silver ions in KCl matrix. During silver doping, no extra peaks corresponding to oxide phases or their compounds were found in spectrum.

**UV-Vis**

The transmission spectra of samples are presented in Fig. 3. It is seen that the crystals are

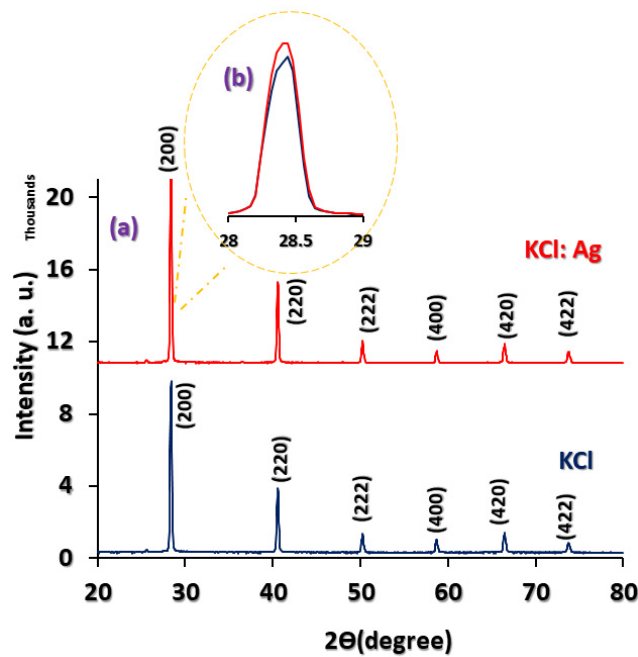


Fig. 2: XRD patterns of pure and doped samples.

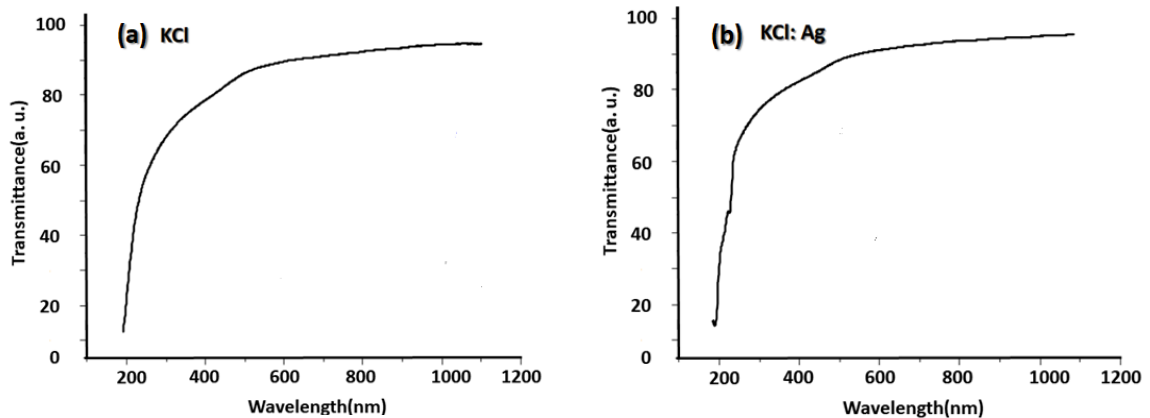


Fig. 3: Transmission spectra of prepared crystals.

transparent in the UV-Vis and near IR regions. This property of crystals makes them suitable candidate to be applied in optical instruments. In Fig. 4, the optical absorption of grown samples is shown. The optical band gap ( $E_g$ ) of crystals was calculated using following equation:  $\alpha h\nu = (h\nu - E_g)^{0.5}$ , where  $\alpha$  is absorption coefficient,  $h\nu$  and  $E_g$  are the photon energy and the optical band gap, respectively. The optical band gap can be measured by extrapolating the linear portion of the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  (to  $\alpha = 0$ ).  $E_g$  is found to be  $\sim 7.5$  eV for KCl and 7.1 eV for KCl: Ag crystal. Wide band gap materials are good candidates for light emitting devices in the short wavelength [9,10].

#### PL, XRIL, TL

Room temperature PL spectra of KCl and KCl: Ag crystals are shown in Fig.5a. Crystal phosphors show a broad emission band at  $\sim 400$ -460 nm and a weak emission peak at 596 nm. The

X-ray induced luminescence curves of samples are shown in Fig.4b. They reveal a broad peak located at 410-450 nm. According to Fig. 5a,b the intensity of blue emission significantly increases for doped crystal; Indeed, the intensity of emission peaks is affected by Ag doping because the energy levels of this additive lie at the different levels of band gap of the host KCl. The blue emission peak centered at 406 nm is attributed to the  $4d^{10} \rightarrow 4d^9 5s$  electronic transitions of  $Ag^+$  ions generally, the blue luminescence peak is related to the localized exciton placed on a pair of Ag and Cl anion. The emission peak at  $\sim 460$  nm can be attributed to the transitions from the excited state of  ${}^3T_{1u}$ . Normally the luminescent emission depends on the kind of activator and its concentration in the host lattice. The luminescent emission is usually originated due to presence of some defects in the host lattice producing certain impurity sites or centers during preparation process. The produced

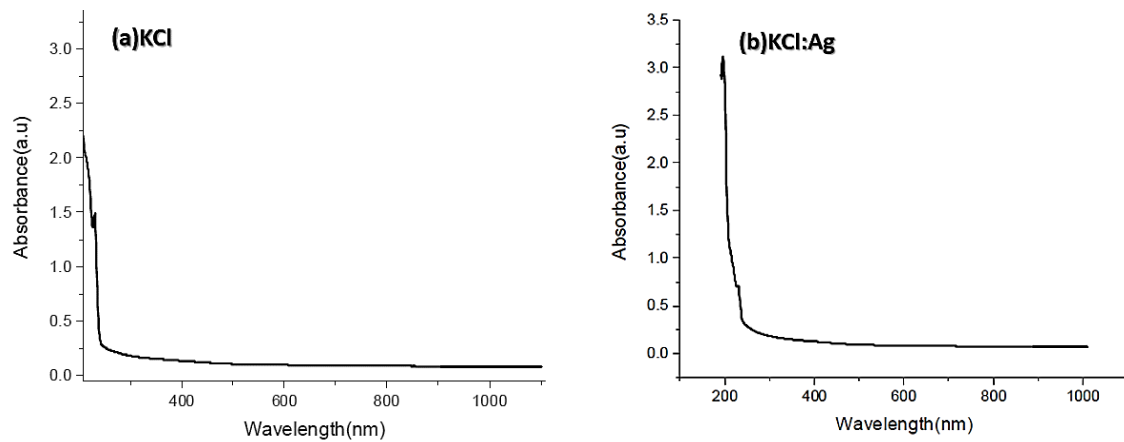


Fig. 4: Absorption spectra of grown crystals.

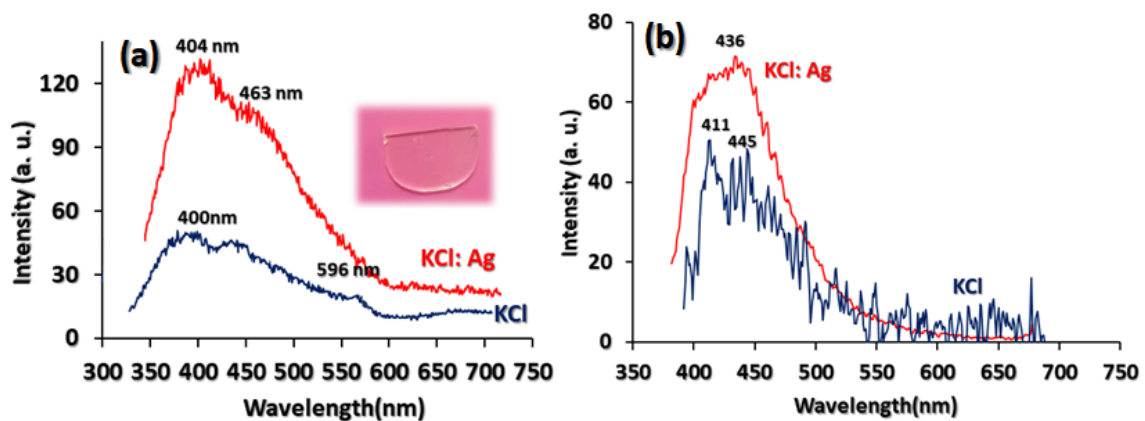


Fig. 5:(a) Room temperature PL and (b)X-ray induced luminescence of crystals

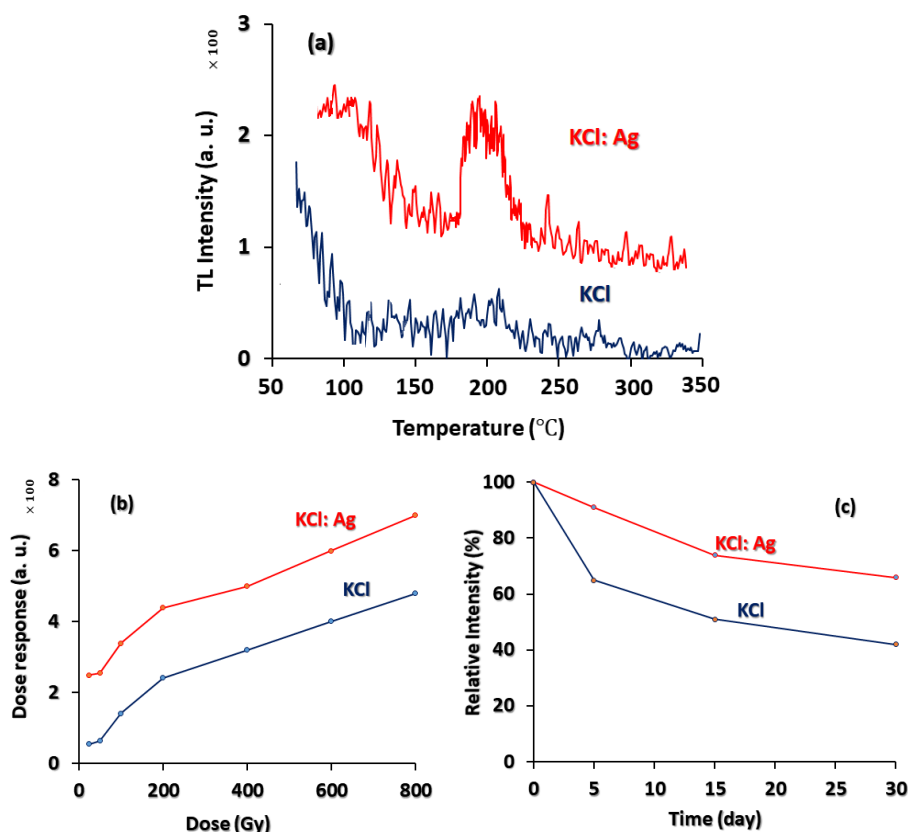


Fig. 6: (a) TL glow curve, (b) TL intensity as a function of dose and (c) Fading of TL intensity versus duration (irradiation source:  $^{60}\text{Co}$ ) of samples.

traps and shallow levels influence the transfer of energy to the luminescent centers. The difference between electron affinity, electronic configuration, ion radius and electronegativity of Ag and host KCl crystal leads to the localized excitons and exhibit different luminescence properties. TL investigation is a powerful technique to study defects in materials with wide applications in the field of radiation dosimetry.

Fig.6a shows the glow curves of gamma radiated pure and doped KCl crystals. The TL spectra consist of a glow peak centered at around 200 $^{\circ}\text{C}$ . It is obvious that sensitivity of doped crystal is more than that of the pure one.  $\text{Cl}^-$  and  $\text{Ag}^+$  ions are very unstable ions which are released during heating and form new hole-centers in the band gap of crystal inducing intrinsic TL emissions. Fig. 6b shows the dose response of samples irradiated by different gamma dose rates and measuring the TL intensity. It is seen that samples have linear behavior between 25 and 800 Gy doses of radiation.

Fig. 6c shows fading percentage of the

thermoluminescence intensity for both samples for duration of 30 days after first measurement. It is seen that the fading intensity decreases by increase of duration. Fading of TL intensity of pure and doped KCl are almost similar to each other, but fading rate of pure crystal is more than that of the doped ones. It can be said that capture of new deep centers is the main reason for this manner. These centers are created by doping of Ag in the crystal lattice of KCl. It is observed that captured charges for doped sample have more thermal stability than pure sample. Silver has  $ns^2$  electronic configuration in the ground state condition ( $^1A_{1g}$ ) and  $ns\ np$  electronic configuration in excited state condition ( $^1T_{1u}$ ,  $^3T_{2u} + ^3E_u$ ,  $^3T_{1u}$ ) which acts as a cation in host material. The Ag impurity center forms especial energy levels in the bandgap of host alkali halide crystal giving rise good luminescence bands due to the electronic transitions between these levels [13, 14]. As can be found from Fig. 7, Ag has smaller electron affinity ( $E_a=1.30\text{ eV}$ ) than that of Cl ( $E_a=3.61\text{ eV}$ ), which can act as a trapped center

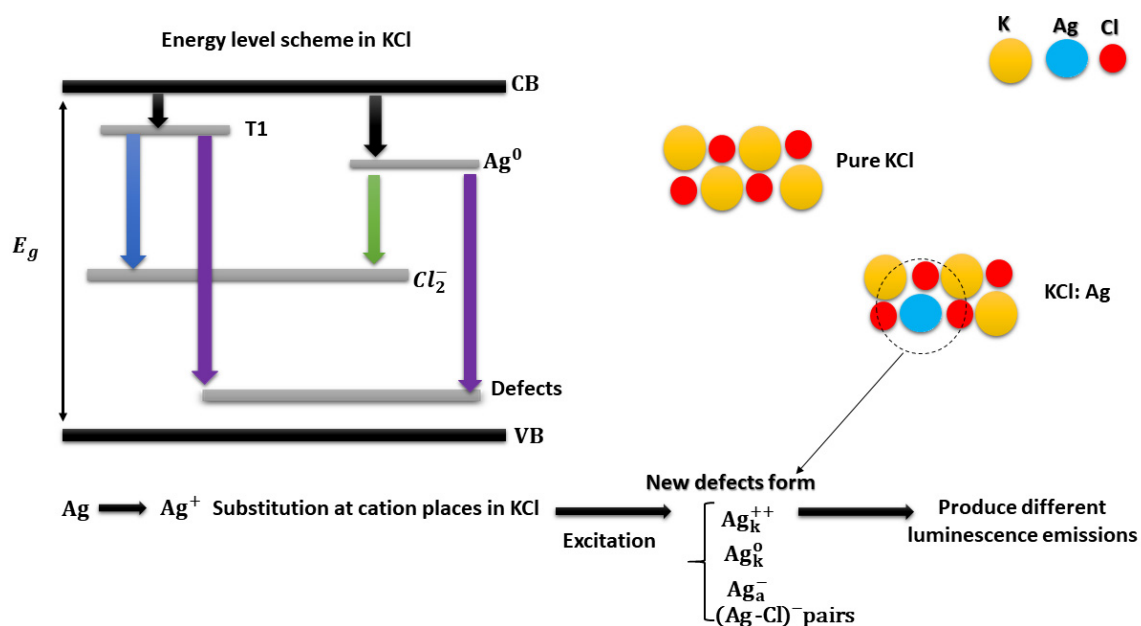


Fig. 7: Energy transfer and generated defects for luminescence properties.

or hole in the band gap of host crystal. During photoexcitation, the silver center grabs the hole and becomes the neutro silver ion.  $\text{Ag}^0$  and  $\text{Cl}^-$  ions are attached to each other and form a new defect of  $(\text{Ag Cl})^-$  leading to blue luminescence [14]. So, it is proposed that a radiative recombination occurs between neighbor  $(\text{Ag -Cl})^-$  pairs (see Fig. 7). The produced traps and shallow levels influence the transfer of energy to the luminescent centers. The difference between electron affinity, electronic configuration, ion radius and electronegativity of Ag and host KCl crystal leads to the localized excitons and exhibits different luminescence properties. The Ag impurity center forms especial energy levels in the bandgap of host alkali halide crystal leading to the good luminescence bands due to the electronic transitions between these levels [16].

## CONCLUSION

Pure KCl and Ag doped KCl crystals were grown using Czochralski method. Prepared crystals showed wide transparency in the entire visible and IR regions. The presence of K, Cl and Ag elements was confirmed by the EDX measurements. Doped crystal exhibited intense thermoluminescence (TL) and luminescence after X-ray and UV irradiation. The luminescence study of Ag doped KCl crystal revealed that it could be used as a scintillator phosphor.

## ACKNOWLEDGMENTS

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## CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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